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IN THE UNITED STATES DISTRICT COURT  
FOR THE NORTHERN DISTRICT OF ILLINOIS  
EASTERN DIVISION

NOV 06 2007  
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MICHAEL W. DOBBINS  
CLERK, U.S. DISTRICT COURT

NALCO COMPANY,  
a Delaware corporation,

Plaintiff,

v.

ENVIRO TECH CHEMICAL SERVICES,  
INC.,  
a California corporation,

Defendant.

)  
) 07CV6293  
) JUDGE HART  
) MAGISTRATE JUDGE COX  
)  
)  
)

JURY DEMANDED

**COMPLAINT FOR INJUNCTIVE AND OTHER RELIEF**

Nalco Company ("Nalco"), a Delaware corporation, Plaintiff, through its attorneys and for its Complaint for Injunctive and Other Relief against, Enviro Tech Chemical Services, Inc. ("Enviro Tech"), a California corporation, states as follows:

**NATURE OF ACTION**

This is an action for patent infringement under the patent laws of the United States, 35 U.S.C. § 101, *et. seq.*, for Enviro Tech's infringement of U.S. Patents Nos. 5,683,654 issued November 4, 1997 (the "'654 Patent"), 6,015,782 issued January 18, 2000 (the "'782 Patent"), 6,037,318 issued March 14, 2000 (the "'318 Patent"), 6,270,722 issued August 7, 2001 (the "'722 Patent") and 6,669,904 issued December 30, 2003 (the "'904 patent"), (herein collectively "the Patents").

### **THE PARTIES**

1. Plaintiff Nalco is a corporation organized and existing under the laws of the state of Delaware, and has a principal place of business at 1601 West Diehl Road, Naperville, Illinois 60563.

2. Upon information and belief, Defendant Enviro Tech is a corporation organized and existing under the laws of the state of California and has a principal place of business at 500 Winmoore Way, Modesto, California 95358.

### **JURISDICTION AND VENUE**

3. This Court has jurisdiction over this matter pursuant to 28 U.S.C. §§ 1331 and 1338(a) in that this matter arises under an Act of Congress relating to patents.

4. Venue is proper in this district pursuant to 28 U.S.C. §§ 1391(b) and (c) and 1400(b) in that, on information and belief, Enviro Tech engaged in one or more acts of infringement within this district, including *inter alia*, infringing one or more of the Patents, which acts are the subject matter of this action.

### **FACTS**

5. Nalco is the owner of all right, title and interest in and to the Patents. Copies of each of the Patents are attached hereto as Exhibits A through E.

6. Nalco has been selling and continues selling within this district and elsewhere one or more products that are made pursuant to the methods and products claimed in the Patents.

7. Upon information and belief, without authority from Nalco, Enviro Tech has infringed one or more claims of the Patents directly by making, using, selling or offering for sale in this district products, including a bromine-based microbiocide known as BromMax, covered

by and/or made in accordance with one or more claims of the Patents. Enviro Tech is also infringing one or more of the Patents by using one or more Internet sites that are publicly accessible to citizens of the State of Illinois to sell or offer for sale within this district products, including BromMax, covered by and/or made in accordance with one or more claims of the Patents.

8. Enviro Tech has notice of its wrongful conduct, as prescribed by 35 U.S.C. § 287.

9. Upon information and belief, Enviro Tech's infringement is willful.

10. Enviro Tech's infringement of the Patents has caused irreparable injury to Nalco, and unless and until Enviro Tech's continuing infringement of the Patents is enjoined by this Court, Nalco will continue to suffer irreparable injury. Nalco has no adequate remedy at law.

#### **PRAYER FOR RELIEF**

WHEREFORE, Nalco prays that this Court enter an Order and Judgment, in their favor and against Enviro Tech:

- (a) preliminarily and permanently enjoining Enviro Tech, and its parents, subsidiaries, affiliates, officers, directors, agents, employees, successors, attorneys and all persons in active concert or participation with them, from infringing the Patents;
- (b) ordering Enviro Tech to pay Nalco the damages that it has incurred as a result of the acts complained of herein, including an award to Nalco of its lost profits as a result of the acts complained of herein, or, in the alternative, an award to Nalco of damages based on a reasonable royalty as a result of the acts complained of herein, and that any such damages award be trebled pursuant to 35 U.S.C. § 284;
- (c) ordering Enviro Tech to pay Nalco prejudgment and post judgment interest on its damages and the costs and expenses of this action, and its reasonable attorneys' fees, as a result of the acts complained of herein; and
- (d) awarding Nalco any other relief that this Court deems just and fit.

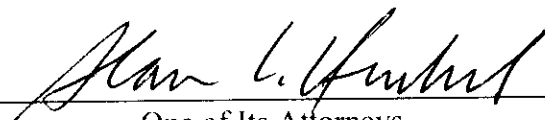
**DEMAND FOR JURY TRIAL**

Pursuant to Fed. R. Civ. P. 38(b), Plaintiffs demand a trial by jury.

DATED: November 6, 2007

Respectfully submitted,

NALCO COMPANY

By:   
One of Its Attorneys

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## **EXHIBIT A**

US005683654A

**United States Patent**

[19]

[11] **Patent Number:****5,683,654****Dallmier et al.**[45] **Date of Patent:****Nov. 4, 1997**

[54] **PROCESS TO MANUFACTURE STABILIZED  
ALKALI OR ALKALINE EARTH METAL  
HYPOBROMITE AND USES THEREOF IN  
WATER TREATMENT TO CONTROL  
MICROBIAL FOULING**

[76] **Inventors:** **Anthony W. Dallmier**, 3440 Victoria  
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[21] **Appl. No.:** **620,978**

[22] **Filed:** **Mar. 22, 1996**

[51] **Int. Cl.<sup>6</sup>** ..... **C23F 11/08**

[52] **U.S. Cl.** ..... **422/14; 8/108.1; 8/109;  
8/129; 8/115.68; 8/115.69; 8/137; 252/94;  
252/186.21; 252/186.36; 252/186.37; 252/187.1;  
423/511; 423/579**

[58] **Field of Search** ..... **422/14; 423/511,  
423/579; 8/107, 108.1, 109, 129, 115.68,  
115.69, 137; 252/94, 186.21, 186.36, 186.37,  
187.1**

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

3,170,883 2/1965 Owen et al. .  
3,328,294 6/1967 Self et al. .  
3,558,503 1/1971 Goodenough et al. .  
3,749,672 7/1973 Golton et al. .

3,767,586 10/1973 Rutkiewicz .  
4,451,376 5/1984 Sharp .  
4,642,194 2/1987 Johnson .  
4,711,724 12/1987 Johnson .  
4,759,852 7/1988 Trulear .  
4,929,424 5/1990 Meier et al. .  
5,424,032 6/1995 Christensen et al. .... 422/14

*Primary Examiner*—Timothy McMahon

[57]

**ABSTRACT**

The invention is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 6; and then,
- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

**52 Claims, No Drawings**

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1

# PROCESS TO MANUFACTURE STABILIZED ALKALI OR ALKALINE EARTH METAL HYPOBROMITE AND USES THEREOF IN WATER TREATMENT TO CONTROL MICROBIAL FOULING

## FIELD OF THE INVENTION

The present invention relates to a method of preparing a stabilized alkali or alkaline earth metal hypobromite to control microbiocouling, more specifically, a stabilized sodium hypobromite solution the characteristics of which include non-volatility, high free halogen residual, lower bromate formation, reduced generation of absorbable organic halogen in process waters, as well as improved anti-microbiocouling performance.

## BACKGROUND OF THE INVENTION

Aqueous solutions of sodium hypochlorite are widely used in cooling water towers, bleaching processes, treatment of recreational waters including swimming pool water, disinfectants, laundry detergents, and industrial biocides including applications in the petroleum industry. However, a major disadvantage of NaOCl is its instability. As is well known in the art, several methods are used to stabilize NaOCl. The Self et al. reference (U.S. Pat. No. 3,328,294) described a continuous process to stabilize hypochlorite with an equal molar ratio of sulfamic acid. This process was improved upon by Rutkiewicz reference (U.S. Pat. No. 3,767,586) who added a buffer which aided in pH control increasing the stability of concentrated solutions.

Bromine has various advantages over chlorine for water treatment such as better performance in high pH or amine environments and a lower volatility. However, sodium hypobromite, the bromine analog to chlorine bleach, is not stable under typical storage conditions, and as such, is not commercially available. Instead, bromine is typically delivered to water treatment systems by various inefficient or inconvenient methods. The art described by either Self et al. or Rutkiewicz does not mention a method to stabilize the well known precarious sodium hypobromite molecule as disclosed within this invention. Also, this disclosure shall improve upon the art of Rutkiewicz by formulating a more stable, concentrated NaOBr solution in the absence of a buffer.

In one such bromine delivery method, NaBr is oxidized in situ by introducing gaseous chlorine or NaOCl into the process water stream. Another technique uses a stable perbromide ( $\text{Br}_3^-$ ) solution containing 30-40% bromine. The perbromide solution releases bromide and bromine when injected into water systems. The formed bromine hydrolyzes instantly to hypobromous and hydrobromic acids. Alternatively, bromine chloride may be added to aqueous process streams wherein it hydrolyzes to hypobromous and hydrochloric acids.

All of these bromine delivery systems have inherent disadvantages. Gaseous chlorine, perbromide, and bromine chloride have high halogen vapor pressures which present safety concerns in handling and storage. Also, these concentrated halogen solutions are corrosive to many metal surfaces found in process equipment either by their high vapor pressures or by the release of one mole of hydrohalic acids in water systems yielding localized low pH environments. As such, none of these methods provide a stable bromine product that can be safely and easily handled while meeting environmental requirements (more fully discussed below), such as low bromate and absorbable organic halogen

2

generation, and having a high free halogen residual and a low volatility (resulting in a greatly reduced odor and vapor-phase corrosion). In addition, a portion of the expensive bromine compound is wasted through an ineffective by-product in some delivery schemes. Thus, the need for a safe, convenient, economical, stable bromine water treatment product remains and is significant.

The Goodenough et al. reference (U.S. Pat. No. 3,558,503), teaches stabilization of bromine using any compound which reacted reversibly with bromine. The disclosed compounds include:

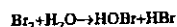
(a) water-soluble primary and secondary amines or amides; and,

(b) sulfamic acid and its water-soluble salts.

However, the bromine solutions prepared according to the Goodenough et al. reference teachings are not stable enough for practical use in commercial cooling water, oil field and other industrial applications.

Sulfamic acid, according to the Goodenough et al. reference, is employed as a free acid or as one of its water-soluble salts such as the sodium, potassium or ammonium salt. However, the manner in which the bromine solutions are prepared provide relatively low stabilities and low available halogen concentrations compared with the discoveries claimed within this invention disclosure. The Goodenough et al. reference charges elemental bromine into aqueous solution prior to stabilization. Because elemental bromine is used in the process disclosed in the Goodenough et al. reference, this process is difficult to complete as well as potentially hazardous since elemental bromine is a fuming, corrosive, toxic liquid.

The Goodenough et al. reference mentions that the available bromine concentration immediately following preparation was about 1% by weight. The low bromine concentration achieved by this method was due in part to bromine being soluble at just 4% in cold water. Additionally, bromine is wasted in the process disclosed in the Goodenough et al. reference. The reaction according to this process is as follows:



Because the produced HBr does not function as a biocide, one half of the bromine adds nothing to the strength of the biocidal species, HOBr. This invention disclosure improves on the Goodenough et al. reference by means of a safer, easier, and more economical process.

Much higher levels of available halogen for disinfection were attained using the invention disclosed in this application, as shown in Table I below, by stabilizing the sodium salt (NaOBr) generated during manufacture. As previously mentioned, sodium hypobromite is unstable and therefore not commercially available. If a stabilized form of NaOBr is proposed, the stabilization process must occur quickly after NaOBr is made.

The method described in the Goodenough et al. reference could not achieve these increased bromine levels as the order of reagent addition described in the reference was deemed not critical to the operability of the method. Since NaOBr is synthesized by the following reaction,  $\text{NaOCl} + \text{NaBr} \rightarrow \text{NaOBr} + \text{NaCl}$ , addition of the stabilizer prior to bromide oxidation would not permit the formation of NaOBr.

When water is treated with many halogenated biocides, undesirable halogenated organics can be generated as by-products. These compounds are causing increased environmental and health concerns. It is generally known that



5,683,654

3

low molecular weight halogenated organics are more easily biologically degraded than higher molecular weight species. However, the low molecular weight forms may be more toxic to aquatic and mammalian organisms. Differentiation of these halogenated organics is costly, time consuming and requires the use of gas chromatography, high performance liquid chromatography or gel permeation chromatography. Absorbable Organic Halogen, "AOX", was chosen as a method of measuring the sum of halogenated organic compounds without speciation. AOX is used as an effluent monitoring parameter of water or wastewater in Europe and North America. In the United States, the Environmental Protection Agency ("EPA") is looking closely at AOX discharge in the pulp and paper industry. An object of the present invention is to provide a stable NaOBr solution that can be used to control microbial fouling with minimal AOX generation. The problems associated with controlling AOX levels, being a more recent developing environmental concern, have not been previously resolved in the industry.

The United States EPA extrapolates some animal carcinogenesis with the presence of low bromate levels found in drinking water. Bromate may appear from the ozonation of bromide-containing water raising some concerns in the drinking water industry. Bromate may also be formed by the disproportionation of hypobromite. This reaction occurs at a greater rate in alkaline environments. Hence, if bleach is added to a NaBr solution, the high pH environment could lead to the undesirable production of bromate. One use of the present invention, which was previously unknown and is surprising, is to greatly minimize bromate formation by stabilizing hypobromite when conditions are favorable for bromate production.

The petroleum industry experiences biological problems, including microbiologically influenced corrosion, both localized and general, in oil field waters. In addition, bacteria can plug the wellbore surface in waterflood injection wells. The bacteria form slime plugs, reducing injectivity. Treatment with stable bromine water is a convenient method of dealing with these and similar problems.

It is an object of the present invention to provide a process whereby aqueous solutions of sodium hypobromite can be produced which are relatively resistant to degradation and/or decomposition and which are relatively non-corrosive and non-volatile, yet which retain an improved capacity for oxidation and bactericidal activity.

Another object of the present invention is to provide a stable sodium hypobromite solution in which the formation of AOX is minimized while providing improved microbial fouling control. Other objects and advantages of the present invention will become obvious from the following description thereof.

#### SUMMARY OF THE INVENTION

The invention, according to one embodiment is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an

4

alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 6; and then,

- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

On embodiment of the invention is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 6; and then,
- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

The alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, magnesium hypochlorite, lithium hypochlorite, and calcium hypochlorite. The bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid. As shown in the examples, in a more preferred embodiment, the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

The aqueous solution of unstabilized alkali or alkaline earth metal hypobromite may contain from about 0.5 to about 30% by weight alkali or alkaline earth metal hypobromite, more preferably from about 1 to about 20% by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15% by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 6, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

Another embodiment of the invention is a stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least



5,683,654

5

50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 6; and then,

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

The alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, magnesium hypochlorite, lithium hypochlorite, and calcium hypochlorite. The bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid. As shown in the examples, in a more preferred embodiment, the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

The aqueous solution of unstabilized alkali or alkaline earth metal hypobromite may contain from about 0.5 to about 30% by weight alkali or alkaline earth metal hypobromite, more preferably from about 1 to about 20% by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15% by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 6, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

The invention can be used in an industrial water system. Such water systems would contain from about 0.05 to about 1000 ppm, more preferably from about 0.05 to about 10 ppm, and most preferably from about 0.1 to about 5 of the stabilized aqueous solution of an alkali or alkaline earth metal hypobromite.

The invention can be used in the laundering of soiled garments where the soiled garments are washed in an aqueous media, such as water, containing a detergent and a bleaching agent. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the bleaching agent.

The invention can also be used in the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the oxidizing agent.

The invention can be used in the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the oxidizing agent.

The invention can be used in the control of microbiofouling occurring on the surfaces of equipment in contact with produced oil field waters. An anti-microbiofouling effective amount of stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be added to the produced oil field waters.

The invention can also be used in the control of microbiofouling in aqueous systems. An effective antimicrobiofouling amount of stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be added to aqueous systems.

In another embodiment, the invention is a method of preventing microbiofouling on the surfaces of equipment in contact with in an industrial water system. The method comprises adding to the aqueous system an anti-

6

microbiologically effective amount of a stabilized sodium hypobromite solution. The stabilized sodium hypobromite solution is prepared by the steps of:

a. Mixing an aqueous solution of sodium hypochlorite with sodium bromide;

b. Allowing the sodium bromide and the sodium hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized sodium hypobromite:

c. Adding to the unstabilized solution of sodium hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to sodium hypobromite of from about 0.5 to about 6; and then.

d. Recovering a stabilized aqueous sodium hypobromite solution.

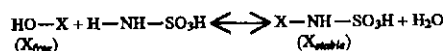
The industrial water systems include cooling water systems, cooling ponds, reservoirs, decorative fountains, industrial pasteurizers, evaporative condensers, hydrostatic sterilizers and retorts, gas scrubber systems, and air washer systems. This invention provides several differences over the known art, including a specific order of addition in the manufacturing process whereby a stabilized sodium hypobromite solution is produced having improved stability, non-volatility, reduced bromate and AOX formation, improved microbiofouling control, and an increased free halogen residual in cooling water.

The stability of the stabilized hypobromite solution, as compared to the stabilized bromine disclosed in the Goodenough et al. reference and unstabilized sodium hypobromite in Table I, is greatly increased. Based on the surprising increased stability of the stabilized sodium hypobromite of this invention, it is apparent that the order of addition in the process of manufacture is critical.

TABLE I

	After 4 days	After 14 days	After 21 days	After 34 days	After 84 days
Goodenough et al.	21	23	—	—	—
Stabilized Sodium	0	0	0	1	1
Hypobromite					
Unstabilized Sodium	—	74	79	84	93
Hypobromite					

The chemical mechanism for halogen biocide stabilization by sulfamic acid has been proposed as follows:



When X is Cl, the reaction applies to stabilized chlorine.  
When X is Br, the reaction applies to stabilized bromine.

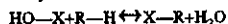
The degree of stabilization is expressed as the concentration ratio of  $X_{stable}$  to  $X_{free}$ . The  $X_{free}$  concentration of the stabilized bromine was detectable while the concentration of the  $X_{free}$  for stabilized chlorine was not. It was concluded that the chlorine in the stabilized chlorine was completely stabilized while the bromine in the stabilized bromine exists in both free and stabilized forms. This contributes in part to the increased antimicrobial properties of stabilized NaOBr over stabilized NaOCl which will be described in more detail in Example 3.

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7

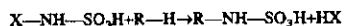
Absorbable organic halogen (AOX) is an important environmental parameter particularly in Europe. AOX can form from the reaction of some halogenated compounds with organics. The minimization of AOX by stabilizing NaOBr is a surprising benefit described in this disclosure.

Pathway A: AOX formation by HOX



Where R—H can be the organic contaminants in cooling water or biomacromolecules and X—R is measured as AOX.

Pathway B:



This stabilized halogen reaction generates no X—R (AOX) as in Pathway A. When free chlorine (HOCl) or free bromine (HOBr) is used, AOX will be formed in accordance with the mechanism described by Pathway A.

When stabilized chlorine is used as a biocide, only Pathway B is possible because no free HOCl exists in the system. Thus, no or very low AOX will be formed using this product (see Table II below).

When stabilized bromine is used, both free and stabilized bromine forms coexist. Thus, both pathways A and B proceed and result in some AOX formation. However, the amount of AOX will be far less than when all of the halogen is in the form of free bromine (HOBr).

Apparently, the proposed mechanism explains the cause of AOX reduction due to the use of stabilized halogen biocides. The mechanism should be applicable to other stabilized halogen products when ammonia, amines or amides are used as the stabilizing agents.

In order to reduce the AOX formation by a stabilized halogen biocide, it is preferable to select strong stabilizing agents so that Pathway B can dominate. However, the drawback to a very stable halogenated compound is the generally decreased oxidation power that, in most cases, is directly correlated to its biocidal efficacy. Testing has shown that stabilized bromine is much more effective as a biocide than stabilized chlorine. Therefore, to reduce the AOX formation and at the same time maintain the compound's biocidal efficacy requires a well balanced selection of the stabilizing agent.

The following examples are presented to describe preferred embodiments and utilities of the invention and are not meant to limit the invention unless otherwise stated in the claims appended hereto.

#### EXAMPLE 1

##### Preparation of Stabilized Sodium Hypobromite with a Critical Order of Addition

In order to demonstrate the constancy of stabilized NaOBr, solutions of sodium hypochlorite and sodium bromide were mixed forming NaOBr then stabilized with sodium sulfamate as described below. Sodium hypochlorite solution was diluted in demand-free water. This diluted solution was titrated by the DPD-FAS method. The available chlorine level present in the original solution was determined to be 15%. 45.7 grams of the neat NaOCl solution were added to 21 grams of a 45% NaBr solution. This reaction forms NaOBr and was allowed to proceed for thirty minutes in the dark. The stabilization solution was formulated with 13 grams of sulfamic acid, 3.1 grams of water, and 17.2 grams of 50% sodium hydroxide. The temperature of the stabilization solution should not be allowed to drop below 50° C. The stabilization solution is then added with

8

stirring to the NaOBr. The order of addition is critical in this process which differs from the Goodenough et al. reference. For instance, if the stabilizer was added to NaOCl prior to NaBr introduction, the bromide would not be oxidized to hypobromite. Also, bromine solutions prepared in the manner referenced above gave more stable oxidizing species than the prior art. Bromine solutions stabilized as explained in the Goodenough et al. reference exhibited a decrease in halogen activity from an initial concentration of 1% to 0.77% after fourteen days representing an active ingredient loss of 23%. The stabilization procedure described here improved on the prior art as the decline of active ingredient was only 1% after 84 days (see Table I above). An unstabilized NaOBr solution prepared in an similar process by replacing sulfamic acid with distilled water lost 94% available halogen during the same period.

#### EXAMPLE 2

##### Less AOX is Formed in Stabilized Halogen Solutions

AOX is a generic class of compounds which includes all organic molecules containing halogen. Limits for AOX discharge from cooling water systems have already been established in some European countries. To simulate AOX formation during stabilized and unstabilized sodium hypobromite action in cooling water, a mixed bacterial culture typically found in cooling water was cultivated in L-broth overnight and the cells harvested by centrifugation. The cell pellet was washed with synthetic cooling water (90 ppm calcium, 50 ppm magnesium, 110 ppm "M" alkalinity, pH 8.0-8.2) twice to remove the remaining organic medium. Cells were then resuspended into an equal volume of cooling water. A capped dark bottle served as the reactor. Synthetic cooling water was added to the bottle followed by the washed bacterial stock yielding approximately  $10^7$  cells/ml. Stabilized NaOBr or unstabilized NaOBr was dosed into this bacterial suspension at a final concentration of 1, 2, 3, or 4 ppm total halogen (as chlorine). Headspace in the bottle was minimized to avoid the evaporative loss of halogenated organics and the solution stirred for 24 hours to simulate a typical cooling system. Immediately before AOX analysis, the sample was acidified to pH 2.0 with concentrated nitric acid. A Mitsubishi TOX-10 Analyzer was used according to US EPA Method 9020 to measure the AOX concentration in the samples. Ultrapure water was used for the preparation of all reagents and standard solutions to prevent any contamination. The amounts of AOX formed in each such treatment is shown in Table II below. Cooling water with stabilized NaOBr formed less AOX than treatments using unstabilized NaOBr at equivalent halogen concentrations. Linear regressions were performed on both sets of data to obtain linear-fit equations shown below for both stabilized and unstabilized NaOBr:

Stabilized NaOBr:  $\text{AOX (ppb)} = 23.3 \times \text{Dose (ppm)}$

Unstabilized NaOBr:  $\text{AOX (ppb)} = 53.9 \times \text{Dose (ppm)}$

Testing also showed that stabilization of NaOCl reduced AOX generation in cooling water dosed with two ppm total residual (see Table II).

5,683,654

9

TABLE II

AOX FORMATION (ppb) IN STABILIZED HALOGEN SOLUTIONS				
DOSE	ppb AOX Formed from Specified Halogen Source			
(ppm total halogen as chlorine)	Stabilized NaOBr	Unstabilized NaOBr	Stabilized NaOCl	Unstabilized NaOCl
1	29	56		
2	52	124	13	118
3	68	174		
4	91	197		

## EXAMPLE 3

## Antibacterial Activity of Stabilized Sodium Hypobromite

Freshly prepared solutions of stabilized and unstabilized sodium hypobromite were diluted then added to cooling water in order to achieve a one ppm free halogen residual (as chlorine). Sodium hypochlorite was stabilized in the same fashion as described for NaOBr in Example One with the exception that NaBr was directly replaced with distilled water. Stabilized and unstabilized sodium hypochlorite were diluted then added to cooling water at a final concentration of one ppm free halogen residual (as chlorine). The volumes of all solutions needed to achieve a one ppm free halogen residual (as chlorine) was recorded. Following 6 and 21 days of dark storage, identical dilutions of stabilized and unstabilized sodium hypochlorite solutions were prepared and the volume originally required for a one ppm free halogen residual (as chlorine) was added to cooling water containing approximately  $10^6$  *Pseudomonas aeruginosa* cells/mL. All-quot were extracted at 10 and 30 minutes into cooling water dilution blanks containing a halogen neutralizer (0.05%  $\text{Na}_2\text{S}_2\text{O}_3$ ) then enumerated on tryprone glucose extract agar. Stabilized NaOBr retained its antibacterial activity after storage while the unstabilized form lost its efficacy against *Pseudomonas aeruginosa* (see Table III below). The results were even more dramatic as the storage period increased. This effect was likely due to the disproportionation of the unstable hypobromite ion into the non-biocidal species bromide and bromate. Surprisingly, NaOCl stabilized in the same manner as NaOBr was comparatively ineffective under the conditions tested (Table III).

TABLE III

ANTIBACTERIAL ACTIVITIES OF STABILIZED & UNSTABILIZED HYPOHALITE SOLUTIONS AFTER 6 & 21 DAYS  
equivalent volumes initially required to achieve one ppm free halogen added throughout test

	% BACTERIA KILLED			
	6 DAYS OF STORAGE		21 DAYS OF STORAGE	
	CONTACT TIME (MINUTES)	CONTACT TIME (MINUTES)	CONTACT TIME (MINUTES)	CONTACT TIME (MINUTES)
	10	30	10	30
stabilized NaOBr	99.9	100	99.8	100
unstabilized NaOBr	99.8	99.7	0.4	6.1
stabilized NaOCl	0	0	0	21.0
unstabilized NaOCl	100	100	100	100

## EXAMPLE 4

Depression of Bromate Formation Following Stabilization of Sodium Hypobromite

10

Hypohalite ions are known to disproportionate into halate and halide under alkaline conditions. Halate ions are undesirable degradants being suspect carcinogens and are under consideration for governmental regulation. The reaction of NaBr with NaOCl can yield significant amounts of bromate in elevated pH environments. Surprisingly, the stabilization of NaOBr with sodium sulfamate greatly minimized bromate formation (see Table IV below). Stabilized and unstabilized sodium hypobromite solutions were prepared as described in Example One. These solutions were stored in the dark at room temperature during the course of the study. Eight month old samples of stabilized and unstabilized NaOBr, both maintained at pH 14, a condition suitable for bromate formation, were assayed for bromate. A Dionex 4000 series gradient ion chromatography system equipped with AG9-SC/AS9-SC columns and a conductivity detector was used to measure the bromate concentration in the samples. The chromatograph was operated according to a method currently under investigation by the EPA for the analysis of bromate in ozonated drinking water. Purified water from an Interlake Water Systems deionization system was used for the preparation of all reagents and standard solutions to prevent contamination.

TABLE IV

BROMATE FORMATION IN STABILIZED & UNSTABILIZED NaOBr SOLUTIONS STORED FOR EIGHT MONTHS

	STABILIZED NaOBr	UNSTABILIZED NaOBr
PERCENT BROMATE	0.004	2.700

As noted above, the pH of these solutions was high which favors bromate formation. However, NaOCl, which contains significant amounts of NaOH, is typically diluted with system water prior to the introduction of the bromide species in most industrial applications. The pH of this diluted system would be lower than the neat NaOCl/NaBr formulation described above theoretically minimizing bromate formation. The available chlorine in a NaOCl sample diluted (1:100) with distilled water was titrated by the DPD-FAS method. A solution of 45% sodium bromide was added to the dilute NaOCl at a molar ratio of 1  $\text{Cl}_2$ : 1 Br forming NaOBr. This reaction proceeded for thirty minutes. Then, appropriate volumes of this dilute NaOBr solution were added to cooling water (pH 8.3) giving total available halogen levels of 1, 2, 3, and 4 ppm (as  $\text{Cl}_2$ ) as determined by the DPD-FAS method. Similarly, a dilution of stabilized sodium hypobromite (1:100) was made in distilled water. Dilute stabilized NaOBr was added to cooling water (pH 8.3) giving total available halogen levels of 1, 2, 3, and 4 ppm (as  $\text{Cl}_2$ ) as determined by the DPD-FAS method. Bromate analysis then proceeded in the manner described above. Bromate was not detected in any of the cooling water samples dosed with either stabilized or unstabilized dilute NaOBr at typical use concentrations. These results signify the safety factor for bromate built into the stabilized sodium hypobromite formulation as well as the industrial in situ oxidation of NaBr with dilute NaOCl.

## EXAMPLE 5

Use of Stabilized NaOBr Increased the Percentage of Free Residual in a Recirculating Cooling Water System Compared to Other Stabilized Halogen Compounds

A major drawback to some commercial stabilized chlorine products for industrial water treatment is the low percentage



5,683,654

11

of free chlorine residual delivered to the water system. This effect is due to the strength of the chemical bond between the stabilizer, usually a nitrogenous compound, and chlorine. Chloramines, i.e. combined chlorine, are weaker microbicides than free chlorine. However, bromamines are considered to be nearly as effective against microorganisms as free bromine. Thus, it is essential to have a high percentage of the total available halogen in the free form when chlorine products are employed. Conversely, this phenomenon is not as crucial when employing stabilized NaOBr. A commercial heating, ventilation and air conditioning ("HVAC") cooling system was sequentially treated with stabilized NaOCl, a bromochloroalkylhydantoin, and finally stabilized NaOBr. There was a low percentage of free chlorine relative to total available halogen present in the stabilized NaOCl treated system (see Table V below). A lower percentage of free halogen was measured when a different stabilization system, an alkylhydantoin, was employed with bromine and chlorine (see Table V below). However, when stabilized NaOBr was fed into this system, the percentage of free available halogen relative to the total residual measured quickly increased (see Table V below). These phenomena imply that less stabilized NaOBr is required to obtain a free available halogen residual than the equivalent amount of stabilized NaOCl.

TABLE V

Free Residual Oxidant as a Percent of Total Residual Oxidant in Recirculating Cooling Water System		
Days in System	Average Free Oxidant as a Percent of Total Residual Oxidant	Biocide Employed
36	13	stabilized NaOCl
45	9	halogenated hydantoins
33	53	stabilized NaOBr

## EXAMPLE SIX

## Stabilization of Sodium Hypobromite Reduces Volatility

If a biocide is highly volatile, its performance may be adversely affected. For example, the biocide may flash off in the highly aerated conditions of a cooling tower or an air washer. This would lower the biocide concentration in the cooling water wasting the product. Halogen volatility also leads to vapor-phase corrosion of susceptible equipment surfaces. In addition, halogen volatility may cause worker discomfort due to the "swimming pool" aroma. Thus, the need for an efficacious oxidizing biocide with low volatility is evident.

Concentrated solutions of either NaOCl, NaOBr, or stabilized NaOBr were added to a beaker. Halogen vapors were detected from the NaOCl and NaOBr solutions. No odors were noticed from the stabilized NaOBr. This is an improvement over existing products by minimizing halogen odors in product storage areas.

Bleach, NaOCl, is not commonly used in air washer systems due to some of the reasons listed above. Once an effective microbial control dose is achieved, the halogen odor may be so overwhelming that workers would not be able to comfortably operate in the treated areas. The low volatilization of stabilized NaOBr overcomes this drawback. Stabilized sodium hypobromite was added at elevated use concentrations to two textile mill air washers in order to investigate its volatility. Then the air was monitored throughout the mill. A Scasidyne air monitoring device outfitted with halogen detection tubes was used to instantaneously detect halogen in the air. The lower detection limit

12

was 50 ppb which is below the Threshold Limit Value-Short Term Exposure Limit for bromine as established by OSHA. In addition, halogen badges were placed throughout textile mills in order to detect halogen vapors over extended periods of time. Neither monitoring system detected any halogen present in the air following the elevated stabilized NaOBr dose. No halogen odors were encountered in either the air washer unit or the return air. The microbial population was enumerated before and after stabilized NaOBr addition. The microbial population following dosing was reduced by greater than one order of magnitude. This example demonstrates the utility of stabilized sodium hypobromite in controlling the bacterial population while adding no halogen odor to the system area.

Changes can be made in the composition, operation and arrangement of the method of the present invention described herein without departing from the concept and scope of the invention as defined in the following claims:

We claim:

1. A method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution comprising:
  - a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;
  - b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
  - c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 6; and then,
  - d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.
2. The method according to claim 1, wherein the alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite, and calcium hypochlorite.
3. The method according to claim 1, wherein the bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid.
4. The method according to claim 1, wherein the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.
5. The method according to claim 1, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 1 to about 20% by weight alkali or alkaline earth metal hypobromite.
6. The method according to claim 1, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 4 to about 15% by weight alkali or alkaline earth metal hypobromite.
7. The method according to claim 4, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 1 to about 20% by weight sodium hypobromite.
8. The method according to claim 4, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 4 to about 15% by weight sodium hypobromite.
9. The method according to claim 7, wherein the pH of the stabilized aqueous sodium hypobromite solution is from about 8 to about 14.

5,683,654

13

10. The method according to claim 8, wherein the pH of the stabilized aqueous sodium hypobromite solution is from about 11 to about 14.

11. The method according to claim 9, wherein the molar ratio of the alkali metal sulfamate to the sodium hypobromite is from about 0.5 to about 4.

12. The method according to claim 10, wherein the molar ratio of the alkali metal sulfamate to the sodium hypobromite is from about 0.5 to about 2.

13. A stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;

b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 6; and then,

d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

14. The solution of claim 13, wherein the alkali or alkaline earth metal hypochlorite is selected from the group consisting of sodium hypochlorite, potassium hypochlorite, lithium hypochlorite, magnesium hypochlorite, and calcium hypochlorite.

15. The solution of claim 13, wherein the bromide ion source is selected from the group consisting of sodium bromide, potassium bromide, lithium bromide, and hydrobromic acid.

16. The solution of claim 13, wherein the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

17. The solution of claim 13, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 1 to about 20% by weight alkali or alkaline earth metal hypobromite.

18. The solution of claim 13, wherein the aqueous solution of unstabilized alkali or alkaline earth metal hypobromite contains from about 4 to about 15% by weight alkali or alkaline earth metal hypobromite.

19. The solution of claim 16, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 1 to about 20% by weight sodium hypobromite.

20. The solution of claim 16, wherein the aqueous solution of unstabilized sodium hypobromite contains from about 4 to about 15% by weight sodium hypobromite.

21. The solution of claim 19, wherein the pH of the stabilized aqueous sodium hypobromite solution is from about 8 to about 14.

22. The solution of claim 20, wherein the pH of the stabilized aqueous sodium hypobromite solution is from about 11 to about 14.

23. The solution of claim 21, wherein the molar ratio of the alkali metal sulfamate to the sodium hypobromite is from about 0.5 to about 4.

24. The solution of claim 22, wherein the molar ratio of the alkali metal sulfamate to the sodium hypobromite is from about 0.5 to about 2.

25. An industrial water system containing from about 0.05 to about 1000 ppm of the solution of claim 13.

14

26. An industrial water system containing from about 0.05 to about 1000 ppm of the solution of claim 16.

27. An industrial water system containing from about 0.05 to about 1000 ppm of the solution of claim 23.

28. An industrial water system containing from about 0.05 to about 1000 ppm of the solution of claim 24.

29. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprises using as the bleaching agent the solution of claim 13.

30. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprises using as the bleaching agent the solution of claim 16.

31. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprises using as the bleaching agent the solution of claim 23.

32. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprises using as the bleaching agent the solution of claim 24.

33. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprises using as the oxidizing agent the solution of claim 13.

34. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprises using as the oxidizing agent the solution of claim 16.

35. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprises using as the oxidizing agent the solution of claim 23.

36. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprises using as the oxidizing agent the solution of claim 24.

37. In a method for the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling, the improvement comprises using as the oxidizing agent the solution of claim 13.

38. In a method for the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling, the improvement comprises using as the oxidizing agent the solution of claim 16.

39. In a method for the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling, the improvement comprises using as the oxidizing agent the solution of claim 23.

40. In a method for the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling, the improvement comprises using as the oxidizing agent the solution of claim 24.

41. In a method for the control of microbiofouling occurring on the surfaces of equipment in contact with produced oil field waters, the improvement comprises adding to the produced oil field waters an anti-microbiofouling effective amount of the solution of claim 13.

42. In a method for the control of microbiofouling occurring on the surfaces of equipment in contact with produced oil field waters, the improvement comprises adding to the produced oil field waters an anti-microbiofouling effective amount of the solution of claim 16.

5,683,654

15

43. In a method for the control of microbiofouling occurring on the surfaces of equipment in contact with produced oil field waters, the improvement comprises adding to the produced oil field waters an anti-microbiofouling effective amount of the solution of claim 23.

44. In a method for the control of microbiofouling occurring on the surfaces of equipment in contact with produced oil field waters, the improvement comprises adding to the produced oil field waters an anti-microbiofouling effective amount of the solution of claim 24.

45. A method of controlling microbiofouling in an aqueous system which comprises adding to the aqueous system an effective, anti-microbiofouling amount of the solution of claim 13.

46. A method of controlling microbiofouling in an aqueous system which comprises adding to the aqueous system an effective, anti-microbiofouling amount of the solution of claim 16.

47. A method of controlling microbiofouling in an aqueous system which comprises adding to the aqueous system an effective, anti-microbiofouling amount of the solution of claim 23.

48. A method of controlling microbiofouling in an aqueous system which comprises adding to the aqueous system an effective, anti-microbiofouling amount of the solution of claim 24.

49. A method of preventing microbiofouling on the surfaces of equipment in contact with in an industrial water

16

system which comprises adding to the aqueous system an anti-microbiologically effective amount of a stabilized sodium hypobromite solution, said solution having been prepared by the steps of:

- 5 a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite with a water soluble bromide ion source;
- 10 b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- 15 c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50° C. in a quantity to provide a molar ratio of sulfamate to hypobromite of from about 0.5 to about 6; and then,
- 20 d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

50. The method according to claim 49, wherein the industrial water system is a cooling water system.

51. The method according to claim 49, wherein the industrial water system is a gas scrubber system.

52. The method according to claim 49, wherein the industrial water system is an air washer system.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 5,683,654

DATED : November 4, 1997

INVENTOR(S) : Anthony W. Dallmier and William F. McCoy

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page, please add:

--Assignee: Nalco Chemical Company, Naperville, Illinois--

Signed and Sealed this  
Seventh Day of July, 1998



Attest:

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks



## **EXHIBIT B**



US006015782A

**United States Patent** [19]  
**Petri et al.**

[11] **Patent Number:** **6,015,782**  
 [45] **Date of Patent:** **Jan. 18, 2000**

[54] **PROCESS FOR MANUFACTURING  
 BLEACHING COMPOSITIONS**

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 Cincinnati, Ohio

[21] Appl. No.: **09/077,794**

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[86] PCT No.: **PCT/US95/15950**

§ 371 Date: **Jun. 5, 1998**

§ 102(e) Date: **Jun. 5, 1998**

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PCT Pub. Date: **Jun. 12, 1997**

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 C11D 7/54

[52] U.S. Cl. .... **510/379**; 510/370; 510/380;  
 510/405; 510/499

[58] Field of Search ..... 510/379, 380,  
 510/381, 370, 405, 499

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*Primary Examiner*—Mark Kopec

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[57] **ABSTRACT**

Process for manufacturing bleaching compositions comprising halogen bleach, a source of bromine and an organic or inorganic derived —NH<sub>2</sub> compound whereby improved bleaching performance is obtained and compositions obtainable by said process.

**20 Claims, No Drawings**

6,015,782

1

## PROCESS FOR MANUFACTURING BLEACHING COMPOSITIONS

### FIELD OF THE INVENTION

The present invention relates to a process for the manufacture of an alkaline bleaching composition comprising halogen bleach, a source of bromine, and an organic or inorganic-NH<sub>2</sub> compound and to the compositions obtainable by this process.

### BACKGROUND OF THE INVENTION

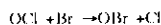
Hard surface cleaners can be in liquid, solid or viscous semi-solid form. Known liquid, solid and viscous semi-solid hard surface cleaners can comprise detergent surfactants, water and optionally certain organic solvents, builders, buffers, and/or perfumes as well as other adjunct materials. Solid and viscous semi-solid forms of hard surface cleaners may optionally comprise as adjunct ingredients one or several abrasive materials. Solid and viscous semi-solid, hard surface cleaners containing abrasive materials are used primarily as "scouring" agents. It has long been known that abrasive materials can be used in conjunction with hard surface cleaners to remove commonly encountered soils or soap scums.

The inclusion of hypochlorite into hard surface cleaners has steadily grown. In fact, hypochlorite-containing hard surface cleaners are among the most effective materials available for cleaning since hypochlorite serves both as a strong oxidizer to assist in the chemical degradation, breakup and removal of stains and soils, and also as an inexpensive and effective disinfectant. This dual role of hypochlorite (as a bleach and disinfectant) together with its shelf stability and compatibility with other optional ingredients has contributed to the increased use of sodium hypochlorite or other positive halogen precursors, in the formulation of hard surface cleaners.

Kitchen and bathroom sink, tub, shower, toilet bowl and counter top surfaces, including vinyl, acrylic, and marble, are areas which have been the focus for developments in increased hard surface cleaning capacity. These surfaces are subject not only to exogenous bacteria, fungi and mildews endemic to most households, but to pathogens which are derived from urine and feces. Therefore, the inclusion of hypochlorite into these formulations as a strong and versatile disinfectant is an added benefit to consumers.

To insure proper hygiene and sanitary conditions, a formidable cleaning task must be undertaken to remove the undissolved sediments, grease, soap films, scums, hard water scale and rust stains that form on ceramic surfaces, counter tops and bathroom floors during normal usage. Cleaning is especially difficult in the case of hardened and dried soap films, scums, caked-on residues and scaling due to hard water/undissolved dirt where it is necessary to use more than simple wiping to remove the unwanted sediments.

It has now been surprisingly found that a bleach composition prepared by a process requiring pre-mixing together a source of bromine such as NaBr with a hypochlorite source, then combining this "pre-mix" with an —NH<sub>2</sub> compound yields a more effective bleaching composition. Without wishing to be limited by theory, it is believed that the following chemical reaction sequence in the pre-mixing step accounts for the formation of hypobromite when the hypochlorite source and the source of bromine are mixed together in the process according to the present invention.



2

Hypobromite, thus formed, being a bleaching agent in itself, is therefore a source of positive halogen and is susceptible to sequestration by the means provided in the present invention. In other words, it is believed that said source of bromine such as sodium bromide has the effect of converting a hypochlorite source into a more reactive and/or a more stable species, for example, hypobromite, thus providing for the full utility of the bleach formulated.

Surprisingly, a combination of an —NH<sub>2</sub> compound, which must be combined with the hypochlorite/bromine premix in a separate step, provides a composition having still more efficacious benefits, for example, the prevention of malodor on human skin when the bleaching compositions obtainable by the present process contact human skin.

There has been a long felt need to combine increased bleaching capacity with other ancillary benefits and for the consumer to obtain these bleaching compositions.

It is thus an object of the present invention to provide bleaching compositions that exhibit improved bleaching performance on the surfaces treated therewith and to have other benefits such as prevention of malodor on human skin as well as superior stability.

### SUMMARY OF THE INVENTION

The present invention encompasses a process for manufacturing a bleaching composition comprising a halogen bleach, a source of bromine and an organic or inorganic derived —NH<sub>2</sub> compound. Said process includes the steps of:

- i) mixing a source of hypochlorite and a source of bromine to form a pre-mix;
- ii) selecting an organic or an inorganic derived —NH<sub>2</sub> compound;
- iii) optionally mixing the selected —NH<sub>2</sub> compound with a carrier or/and an optional ingredient to form an —NH<sub>2</sub> composition; and
- iv) combining the pre-mix from step (i) with the —NH<sub>2</sub> compound of step

(ii) or the —NH<sub>2</sub> composition of step (iii) to form a bleaching composition, wherein the pH of the bleaching composition is greater than 11.

It is an object of the present invention to provide a process for preparing bleaching compositions having a greater bleaching effectiveness.

It is also an object of the present invention to provide a process resulting in a bleaching composition having increased stability and shelf life.

It is a further object of the present invention to provide bleaching compositions that control malodor formation on human skin when the bleaching compositions come into contact with human skin.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (° C.) unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for manufacturing bleaching compositions having improved efficacy against bleachable stains. The process according to the present invention can be summarized as comprising the following steps.

6,015,782

3

Step (i)—comprises a mixing step wherein a source of hypochlorite and a source of bromine are combined to form a pre-mix.

An essential ingredient of the present invention is the inclusion in step (i) of a suitable hypochlorite source. By "hypochlorite source" it is meant herein alkali metal or alkali earth metal hypochlorites, as well as alternative hypochlorite sources like hypochlorous acid, or chlorine or even organically derived sources of hypochlorite such as chloroisocyanurate. Preferred hypochlorite sources are according to the formula  $M(OX)_y$ , where: M is a member selected from the group consisting of sodium, potassium, magnesium, calcium, and mixtures thereof; O is an oxygen atom; X is a chlorine; and y is 1 or 2 depending on the charge of M. Particularly preferred hypochlorite source to be used according to the present invention are sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, and magnesium hypochlorite, and more preferably sodium hypochlorite.

The concentration level of hypochlorite in step (i) is not restricted to the levels commercially available to the formulator but may also comprise concentrations produced by a manufacturing-site process, for example, the passing of chlorine gas into an alkaline aqueous solution. The latter process example, depending upon the choice of alkali, allows the formulator to incorporate selected cations (e.g.  $K^+$ ,  $Ca^{2+}$ ) into the final formulation.

A further essential ingredient of the present invention is the inclusion in step (i) of the present process of a source of bromine. For the purposes of the present invention the term "source of bromine" is defined as "any material, whether organic or inorganic, used alone or otherwise in combination with other organic or inorganic materials comprising bromine, that serve as a source of bromide ion when the source of bromine is contacted with a suitable source of hypochlorite under the conditions of step (i) of the present invention". When this suitable source of bromine is mixed with the source of hypochlorite in step (i) a hypohalite species is formed which will subsequently undergo mediation by the  $-NH_2$  material of steps (ii) or (iii). The formulator may select elemental bromine ( $Br_2$ ), organic bromides such as N-bromosuccinimide, as well as pre-formed NaOBr and  $Br^-$  yielding salts (e.g. NaBr) for use in this process. Suitable  $Br^-$  yielding salts are according to the formula  $M(X)_y$ , where: a) M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, zinc, and mixtures thereof, and b) X is the radical bromide, bromate, and mixtures thereof, wherein y is 1 or 2. Particularly preferred  $Br^-$  yielding salts are of the formula MX where M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, and zinc while the X is Br. Thus the preferred  $Br^-$  yielding salts are the sodium and potassium salts of bromine, more preferably sodium and potassium bromide. For the purposes of the present invention, it is not important that at the time of forming the admixture in step (i) that all bromine have the same form. Some or all bromine may be added as  $Br^-$ .

Alternatively, chemical equilibrium can be used to establish the level and forms of available bromine. Therefore the formulator may choose to have all available bromine in a chemically combined form upon admixture with the source of hypochlorite in step (i) and thereby use the intrinsic equilibrium of the system to establish the level of  $Br^-$ .

Step (ii)—comprises selecting an organic or an inorganic derived  $-NH_2$  compound.

4

A further essential ingredient of the present invention is the inclusion in step (ii) of the present process of an organic or inorganic derived  $-NH_2$  compound. For the purposes of the present invention, the term "organic or inorganic derived  $-NH_2$  compound" is defined as any  $-NH_2$  material alone or in combination with other suitable  $-NH_2$  compounds other than ammonia ( $NH_3$ ) or salts thereof (e.g.  $NH_4Cl$ ), that provide a source of hypohalite mediation. Not wishing to be limited by theory, the mediation by the  $-NH_2$  compounds of the hypohalite species formed by the admixture of the hypochlorite and bromine compounds of step (i) of the present process, produces a product with superior bleaching performance and provides for the control of malodor formation on human skin.

Compounds suitable for selection as  $-NH_2$  compounds in step (ii) of the present invention are those which, in their reaction with hypochlorous acid, favor N-bound chlorine over free chlorine or O-bound chlorine. Preferred  $-NH_2$  compounds include  $-NH_2$  compounds that have a characteristic hydrolysis constant,  $K_H$ , for the corresponding chloramine. This hydrolysis constant is given by:

$$K_H = \frac{[HOCl][RNH_2]}{[RNHCl]}$$

wherein  $K_H$  is in the range from about  $10^{-6}$  to about  $10^{-9}$ .

The corresponding hydrolysis reaction of the chloramine is given by:



this reaction being the equilibrium result of adding to a sample of pure water the chloramine  $RNHCl$  derived from the selected  $-NH_2$  compound,  $RNH_2$ .

In the above, R denotes an organic or inorganic group other than H, consistent with the definition of the essential  $-NH_2$  compound. R can, for example, be a moiety  $-HSO_3$ , in which case  $RNH_2$  is sulfamic acid.

Hydrolysis constants such as the above are well known in the art and are defined conventionally. See, for example, Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 5, article entitled "Chloramines and Bromamines", see especially page 567, and Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 3, see especially pages 940-941, said articles being incorporated herein by reference.

$-NH_2$  Compounds respecting the above relationship include sulfamic acid, which is a preferred  $-NH_2$  compound herein; in contrast, and for purposes of comparison, isocyanuric acid and the corresponding chloroisocyanurates do not respect the above relationship and thus, while use of isocyanurates is permitted as an optional ingredient (e.g. a source of hypochlorite), they cannot be used as the essential  $-NH_2$  compound herein.

Examples of said  $-NH_2$  compounds are sulphamic acid, sulphamide, p-toluenesulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamides, and mixtures thereof. Particularly preferred herein are sulphamic acid, sulphamide or mixtures thereof. At pH levels of the present invention, which are greater than 11, the above mentioned  $-NH_2$  compounds may be de-protonated, that is they may be in the form of a salt and therefore due to expediency, ease of synthesis or preparation, or due to formulation practices the salt form of any or all of the above mentioned  $-NH_2$  compounds will suffice. Although any suitable cation will suffice for the purposes of the present invention, sodium, potassium, lithium, magnesium, calcium, and mixtures thereof are preferred.

6,015,782

5

Step (iii)—comprises a step which allows the formulator the ability to pre-combine any suitable adjunct ingredients or carriers with the selected  $\text{—NH}_2$  compound prior to combining the  $\text{—NH}_2$  compound with the pre-mix that is formed in step (i).

Step (iv)—comprises a step wherein the pre-mix obtained in step (i) of the present invention is combined with the  $\text{—NH}_2$  compound that was selected in step (ii) or alternatively the  $\text{—NH}_2$  composition (which includes adjuncts and carriers) that was pre-combined in step (ii). The resulting solution has a final pH of greater than 11 and is an improved bleaching composition.

Step (iv) according to the process of the present invention may be followed by further steps for example, a dilution step. Typically for better storage stability, such a dilution step is not carried out in the plant, but it may be carried out by the consumer who uses the composition. Dilution can result in pH variation, typically including pH decrease.

According to the present invention the process conditions generally applicable are those generally known by those skilled in the art. Thus, mixing can be accomplished using any convenient means such as a magnetic or mechanically driven stirrer. Typical step reaction times can be in the range from about 1 minute to about 2 hours depending on mixing scale.

The present process is typically performed at a temperature range from about  $5^\circ\text{C}$ . to about  $80^\circ\text{C}$ ., preferably from about  $10$  to about  $45^\circ\text{C}$ . and more preferably at ambient temperature. At higher temperatures, there may be an increased decomposition tendency and at lower temperatures, freezing can be a problem.

By the process of the present invention, step (i) and steps (ii) and (iii), can be carried out in any order, i.e. (i) before (ii) and (iii), or (ii) and (iii) before (i), provided that step (ii) is always performed before step (iii). Also it is essential that said steps are followed by step (iv), i.e. by combining the pre-mix resulting from step (i) with the  $\text{—NH}_2$  compound of step (ii) or the  $\text{—NH}_2$  composition of step (iii) to form a bleaching composition.

Each of the steps (i) and (iii), can have one or more mixing steps. Indeed there may be pre-processing steps, such as dissolving solids in water if the raw materials are available in solid form. The process according to the present invention may also include post-processing steps, such as diluting the composition resulting from step (iv).

In the embodiment of the present invention wherein the compositions obtainable according to the process of the present invention further comprise one or more optional ingredient as mentioned herein after, said ingredients may be added into the compositions step (iii) or added thereafter. Non-limiting examples of bleaching compositions that are further modified after step (iv) are, for example, a bleaching composition that is diluted with water prior to packaging or a bleaching composition wherein an inert material, such as an abrasive is added. Also step (iii) may comprise one or more steps of mixing said organic or inorganic derived  $\text{—NH}_2$  compound with said carrier and/or said optional ingredient.

Steps (i) and (iii) are carried out preferably in presence of a carrier. By "carrier" it is meant herein any carrier known to those skilled in the art including solid and/or liquids, for example, water.

In the present invention it is essential that the process comprises said pre-mix step wherein said hypochlorite source is mixed together with said source of bromine separately from said organic or inorganic derived  $\text{—NH}_2$  compounds. Without being limited by theory, it is believed that the order

6

of combining ingredients, that is, first combining a source of hypochlorite with a source of bromine prior to combining with an  $\text{—NH}_2$  compound is essential to producing a bleaching composition with increased efficacy.

For the purposes of the present invention, "improved bleaching" is meant herein that a bleaching composition obtainable by the process of the present invention delivers better bleaching performance on bleachable stains, for example, tea stains, when compared to the bleaching performance delivered by the same composition made by an alternative process, for example by a process comprising the steps of: (a) predissolving said  $\text{—NH}_2$  compound with said source of bromine; (b) mixing the mixture of (a) with the remaining components of the composition not including a hypochlorite halogen bleach; (c) adding NaOH to raise pH to about 13.0, and (d) combining a hypochlorite halogen bleach and the mixture from (c), by adding the hypochlorite to the mixture of (c).

The present invention comprises organic or inorganic derived  $\text{—NH}_2$  compound as a means for controlling malodor or "bleached hand smell" on the skin. While not intending to be limited by theory, the principle component of "Bleached Hand" malodor on the skin is 1-pyrroline. This material is formed from the amino acid L-proline when the keratin protein found in the stratum corneum layers of the skin is exposed to free positive halogen, especially positive chlorine. The rate of formation and the amount of 1-pyrroline that is formed varies from individual to individual but the general mechanism of formation is believed to be universal. The degradation of skin protein is believed to begin with the rapid halogenation of a protein amide bond nitrogen when the skin is exposed to solutions containing hypohalite. If this N-halogenation occurs adjacent to the amino acid L-proline, the ensuing protein fragmentation results in the formation of 1-pyrroline. The rate of protein degradation, once the N-halogenation has occurred is variable from individual to individual and, in some cases, formation of malodor on the skin continues for several days after exposure to "free available halogen".

The present invention also encompasses hard surface cleaning compositions obtainable according to the present process, the compositions comprising a halogen bleach, a source of bromine and an organic or inorganic derived  $\text{—NH}_2$  compound. The compositions obtainable according to said process can be formulated in a variety of different embodiments, especially as household cleaners.

The compositions obtainable by the process of the present invention comprise from about 0.01% to about 10% of said halogen bleach or mixtures thereof, expressed as available chlorine ( $\text{AVCl}_2$ ), preferably about 0.01% to about 5%, more preferably from about 0.1% to about 2.5%, most preferably from about 0.5% to about 2.5%, by weight.

The compositions obtainable according to the process of the present invention comprise said source of bromine or mixtures thereof that are present such that the mole ratio of halogen bleach to said source of bromine is from about 1:0.1 to about 1:2, preferably from about 1:0.2 to about 1:1.

The compositions obtainable according to the process of the present invention comprise said organic or inorganic derived  $\text{—NH}_2$  compound or mixtures thereof such that the mole ratio of halogen bleach to said organic or inorganic derived  $\text{—NH}_2$  compound is from about 10:1 to about 1:10, preferably from about 5:1 to about 1:2, more preferably from about 3:1 to about 1:2.

A preferred embodiment of the present invention encompasses a process of manufacturing a bleaching composition comprising the steps of:



6,015,782

7

- i) mixing at a temperature from about 5° C. to about 80° C. a source of hypochlorite and a source of bromine to form a pre-mix;
  - ii) selecting an organic or an inorganic derived  $\text{—NH}_2$  compound;
  - iii) optionally mixing at a temperature from about 5° C. to about 80° C. the selected  $\text{—NH}_2$  compound with a carrier or/and an optional ingredient to form an  $\text{—NH}_2$  composition; and
  - iv) combining the pre-mix from step (i) with the  $\text{—NH}_2$  compound of step
- (ii) or the  $\text{—NH}_2$  composition of step (iii) to form a bleaching composition, wherein the pH of the bleaching composition is greater than 11.

The process of the present invention has several advantages. The pre-mix obtained in step (i) of the present process can be simultaneously metered into several compositions, each a different embodiment of the present invention. For example, a first feed line may direct the pre-mix obtained in step (i) for combination with a selected  $\text{—NH}_2$  compound obtained in step (ii) while a second feed line directs the pre-mix of step (i) to a  $\text{—NH}_2$  composition derived from step (iii) of the present process comprising detergent surfactant, buffers, builders, and other optional ingredients or carriers. Another advantage is the flexibility it affords the bleaching composition formulator. Indeed the process of the present invention can be conveniently conducted in a single manufacturing location as well as in different locations. It is thus possible to have at least part of the process carried out in more than one location, for example to reduce the cost of shipping water. In this mode, for example, a stable pre-mix composition according to step (1) can be transported safely from one location to second location where the final formulation is accomplished.

A further advantage of the process of the present invention is the usage of alternative forms of bromine, for example, the instant process can utilize elemental bromine ( $\text{Br}_2$ ), salts (i.e.  $\text{NaBr}$ ), as well as suitable organic bromides (i.e. N-bromo-succinimide) and the like. Another advantage of the process of the present invention is the use of any source of hypochlorite. The concentration level of hypochlorite in step (i) is not restricted to the levels commercially available to the formulator but may also comprise concentrations produced by a manufacturing-site process, for example, the passing of chlorine gas into an alkaline aqueous solution. The latter process example, depending upon the choice of alkali, allows the formulator to incorporate selected cations (e.g.  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) into the final formulation.

An advantage of said compositions obtainable according to the process of the present invention is that they can be applied to hard surfaces to be cleaned or bleached using any convenient method of application.

Another advantage of the compositions obtainable according to the process of the present invention is that they can be provided in various forms including any convenient form, e.g., solid, semi-solid, gel or paste or liquid.

Yet another advantage of the present invention is that bleaching compositions are provided which not only exhibit excellent bleaching performance but which also reduce chlorine bleach malodor on the skin. Indeed, the compositions obtainable according to the process of the present invention because of their effectiveness in controlling hypochlorite derived malodor on the skin, preclude the necessity of gloves or other protection of the exposed skin during cleaning.

The compositions obtainable according to the process of the present invention may further comprise optional

8

ingredients, e.g., one or more detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the surface to be cleaned, or to modify the aesthetics of the composition (e.g., perfumes, colorants, dyes, etc.). The conventional optional ingredients to be used in the compositions obtainable according to the process of the present invention further include surfactants, bleach stabilizers, pigments, color speckles, suds boosters, suds suppressers, anti-tarnish and/or anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal/anti-redeposition agents, polymeric dispersing agents and the like and mixtures thereof. The following are illustrative examples of such optional ingredients but are not meant to be exclusive or limiting in scope.

The compositions obtainable according to the process herein have a pH greater than 11, preferably at least 12 and most preferably at least 13. Accordingly said compositions obtainable according to the present invention preferably comprise a pH-adjusting agent such as common mineral acids or bases. Suitable pH adjusting agents to be used herein include any convenient alkaline pH adjusting agent. However it is essential throughout the present process that alkaline pH adjusting agent is non-reactive with hypochlorite. Preferred alkaline pH adjusting agents include water-soluble alkalis such as sodium hydroxide, potassium hydroxide or mixtures thereof. It is preferable herein not to use ammonia which is an example of a generally unsuitable pH-adjusting agent because it is chemically reactive for purposes other than pH change and forms an undesirable type of chloramine with hypochlorite.

The compositions obtainable according to the process herein may comprise from about 0.1% to about 95% by weight of a surfactant or mixtures thereof selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic surface active agents. For liquid systems, surfactant is preferably present to the extent of from about 0.1% to 20% by weight of the composition. For solid (i.e. granular) and viscous semi-solid (i.e. gelatinous, pastes, etc.) systems, surfactant is preferably present to the extent of from about 1.5% to 30% by weight of the composition.

Anionic surfactants can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C8–18 carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid ester of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the

6,015,782

9

reaction products of fatty acids are derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, secondary alkyl sulfates may be used by the formulator exclusively or in conjunction with other surfactant materials and the following identifies and illustrates the differences between sulfated surfactants and otherwise conventional alkyl sulfate surfactants. Non-limiting examples of such ingredients are as follows.

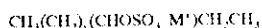
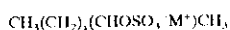
Conventional primary alkyl sulfates, such as those illustrated above, have the general formula  $\text{ROSO}_3\text{-M}^+$  wherein R is typically a linear  $\text{C}_8\text{-C}_{22}$  hydrocarbon group and M is a water solubilizing cation. Branched chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms are also known; see, for example, Eur. Pat. Appl. 439,316, Smith et al., filed Jan. 21, 1991.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbon "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of m+n is typically about 9 to 17, and M is a water-solubilizing cation.

In addition, the selected secondary (2,3) alkyl sulfate surfactants used herein may comprise structures of formulas I and II



for the 2-sulfate and 3-sulfate, respectively. Mixtures of the 2- and 3-sulfate can be used herein. In formulas I and II, x and (y+1) are, respectively, integers of at least about 6, and can range from about 7 to about 20, preferably about 10 to about 16. M is a cation, such as an alkali metal, ammonium, alkanolammonium, triethanol-ammonium, potassium, ammonium, and the like, can also be used.

The aforementioned secondary alkyl sulfates are those prepared by the addition of  $\text{H}_2\text{SO}_4$  to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued Feb. 8, 1966 or in U.S. Pat. No. 5,075,041, Lutz, issued Dec. 24, 1991. The synthesis conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products which, when purified to remove the unreacted materials, randomly sulfated materials, unsulfated by-products such as C10 and higher alcohols, secondary olefin sulfonates, and the like, are typically 90+% pure mixtures of 2- and 3-sulfated materials (some sodium sulfate may be present) and are white, non tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5% of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available as under the name "DAN", e.g., "DAN 200" from Shell Oil Company.

The compositions obtainable according to the process of the present invention which are formulated in a solid or viscous semi-solid form may further comprise an abrasive material, said material may facilitate the action of scouring. Abrasive scouring cleansers provide a convenient and useful means for carrying out the sanitizing of porcelain and tile surfaces, especially tubs, showers and toilet bowls. The particulate abrasive material within such compositions

10

serves to abrade and loosen soil adhering to hard surfaces and further serves to create more intimate contact between hard surface stain and the surfactant and/or bleaching agents also present in the cleansing compositions. Abrasive cleaners have traditionally contained water-insoluble, relatively hard, particulate mineral material as the abrasive agent. The most common such abrasive agent is finely divided silica sand having particle size varying between about 1 and 300 microns and specific gravity of about 2.1 or higher. While such material is generally very effective in scouring soil and stains from the surfaces being treated, abrasive material of this type tends to be difficult to rinse away from the toilet bowl, shower or bathtub surface. It has been discovered that abrasive compositions of this desired type can be realized by utilizing a particular type of expanded perlite abrasive in combination with the surfactants, filler material, and other optional scouring material ingredients listed herein. The abrasive materials suitable to the present invention are those contained in U.S. Pat. No. 4,051,056, Hartman, issued Sep. 27, 1977 and included herein by reference.

Other optional ingredients to be used herein include buffers. One such purpose is to adjust the cleaning surface pH to optimize the hard surface cleaner composition effectiveness relative to a particular type of soil or stain. Buffers may be included to stabilize the adjunct ingredients with respect to extended shelf life or for the purpose of maintaining compatibility between various aesthetic ingredients. The hard surface cleaner of the present invention optionally contains buffers to adjust the pH in a range above 11. Non-limiting examples of such suitable buffers are potassium carbonate, sodium carbonate, and trisodium phosphate, however, the formulator is not restricted to these examples or combinations thereof.

The cleaning compositions obtainable according to the process of the present invention may also optionally contain one or more iron and/or manganese chelating agents. Examples of such compatible chelating agents are ethane-1-hydroxy-1,1-diphosphonic acid (EHDP) and dipicolinic acid.

Perfumes are also an important optional ingredient especially for the liquid composition embodiment. Perfume is usually used at levels of from 0% to 5%. In U.S. Pat. No. 4,246,129, Kacher, issued Jan. 20, 1981 (incorporated herein by reference), certain perfume materials are disclosed which perform the added function reducing the solubility of anionic sulfonate and sulfate surfactants.

The compositions obtainable according to the present invention may be formulated either as solids or liquids, but are preferably used in a liquid form to household cleaning application. In the case where the compositions are formulated as solids, they will thus be mixed with an appropriate solvent, typically water, before use. In liquid form, the compositions are preferably but not necessarily formulated as aqueous compositions. Also suitable carriers for the present invention are water and volatile solvents that are compatible with hypohalite. The liquid compositions obtainable according to the process of the present invention may be formulated with different viscosities. In one embodiment of the present invention the compositions obtainable with the process herein have a viscosity of from about 1 to about 150 cps. Said compositions are convenient for spray bottle application. Likewise, said liquid compositions obtainable according to the present invention can be further thickened, e.g., by the addition of additional bleach-stable thickener, such as the commercially available DOWIAX. A suitable gel formulation has a viscosity of from about 100 cps to about 2000 cps, preferably from 300 cps to 1000 cps as



6,015,782

11

measured, for example, by techniques and methods described in "Physico-Chemical Methods", Reilly, J. and Rac, W. N.; Vol. I (5th ed.), pages 667-692; D. Van Nostran pub.

## EXAMPLES

The following compositions were made by the listed ingredients in the listed proportion according to the process of the present invention.

All percentages herein are percentages by weight on an anhydrous basis, unless otherwise noted.

Component	Example No.						
	1	2	3	4	5	6	7
surfactant	0.25	3.5	5.5	6.5	6.1	6.0	5.2
sulphamic acid	1.30	1.9	2.2	---	---	2.5	2.3
sodium sulfamate	---	---	---	0.5	---	---	---
melamine	---	---	---	---	0.23	---	---
sodium hypochlorite	0.9	1.4	1.4	---	---	1.7	1.5
calcium hypochlorite	---	---	---	0.5	---	---	---
sodium	---	---	---	---	1.2	---	---
dichlorocyanurate	---	---	---	---	---	---	---
tetrapotassium	6.0	---	---	---	13.0	---	---
pyrophos.	---	---	---	---	---	---	---
tripotassium phosphate	2.0	---	---	---	12.0	---	---
sodium	---	---	---	1.6	---	---	---
tripolyphosphate	---	0.04	0.05	---	0.5	0.1	0.2
sodium silicate	---	0.01	---	---	---	---	0.05
sodium periodate	---	---	---	0.3	---	---	---
sodium acetate	---	---	---	---	---	---	---
sodium bromide	---	1.8	1.5	---	---	0.5	0.6
sodium iodide	---	---	0.03	---	---	---	---
potassium bromide	1.1	---	1.1	1.5	1.0	---	---
perfume	---	0.28	0.1	---	---	0.3	0.35
calcium carbonate	---	---	---	---	39.0	---	---
calcium oxide	---	---	---	---	2.8	---	---
perlite abrasive	6.5	---	---	---	22.5	---	---
sodium hydroxide	0.8	1.6	1.8	0.8	1.1	2.8	2.6
potassium hydroxide	---	---	---	0.85	---	---	---
dyes	0.75	0.28	0.28	0.28	---	---	0.01
miscellaneous	---	---	0.02	---	---	---	---
moisture/distilled	bal.	bal.	bal.	bal.	bal.	bal.	bal.
water	---	---	---	---	---	---	---

All the compositions herein obtainable according to the process of the present invention delivered excellent bleaching property when used to treat surfaces as well as reduced chlorine bleach malodor on the skin.

The following processes illustrating the present invention were carried out at room temperature. All the percentages are percentages by weight of the finished compositions obtainable according to the process of the present invention unless otherwise indicated:

In process A a pre-mix is formed (ph=13) by combining Na hypochlorite (15% solution in water) together with NaBr in amounts sufficient to provide respectively 1.4% and 0.5% in the finished composition (step (i)). Sulfamic acid is selected as the  $\text{—NH}_2$  compound and combined with adjunct ingredients to form an  $\text{—NH}_2$  composition comprising water (balance), NaOH (2.4%), 3 ratio Na Silicate (0.4%), sulfamic Acid (2.2%), surfactants (C8AS, C12 Amine Oxide and C16 Amine Oxide at 1.1%, 2.4% and 0.1% respectively), perfume (0.2%) and dye (0.0046%) (step (ii) and (iii)). The pre-mix is then combined with the  $\text{—NH}_2$  composition to form a bleaching composition having a final pH of 13.1.

In process B a pre-mix is formed (ph=12.8) by combining Na hypochlorite (15% solution in water) together with a 40% NaBr solution in water, in amounts sufficient to provide

12

respectively 1.7% and 0.5% in the finished composition (step (i)). Sulfamic acid is selected as the  $\text{—NH}_2$  compound and combined with optional ingredients to form an  $\text{—NH}_2$  composition comprising water (balance), NaOH (3.0%), 3 ratio Na Silicate (0.05%), sulfamic Acid (2.5%), surfactants (C8AS, C12 AS at 4.0%, and 2.0% respectively), and perfume (0.3%). The pre-mix is then combined with the  $\text{—NH}_2$  composition to form a bleaching composition having a final pH of 13.2.

What is claimed is:

1. A process for manufacturing a liquid bleaching composition, said process comprising the steps of:

i) mixing a source of hypochlorite and a source of bromide to form a pre-mix;

ii) selecting an organic or an inorganic derived  $\text{—NH}_2$  compound;

iii) optionally mixing the selected  $\text{—NH}_2$  compound with one or more carriers and/or one or more adjunct ingredients to form an  $\text{—NH}_2$  containing composition; and  
iv) combining the pre-mix from step (i) with the  $\text{—NH}_2$  compound of step (ii) or the  $\text{—NH}_2$  composition of step (iii) to form a bleaching composition;

wherein the pH of said bleaching composition is greater than 11.

2. A process according to claim 1 wherein said source of hypochlorite is selected from the group consisting of alkali metal hypochlorite, alkaline earth metal hypochlorite, hypochlorous acid, chlorine, chloroisocyanurate, and mixtures thereof.

3. A process according to claim 1 wherein said source of bromide is selected from the group consisting of  $\text{Br}_2$ , NaOBr, a salt having the formula  $\text{M(X)}_y$ , wherein M is selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, zinc, or mixtures thereof; X is selected from the group consisting of bromide, bromate, or mixtures thereof; y is 1 or 2; and mixtures thereof.

4. A process according to claim 3 wherein said source of bromide is sodium bromide.

5. A process according to claim 1 wherein said  $\text{—NH}_2$  compound is selected from the group consisting of sulphamic acid, sodium sulphamate, potassium sulphamate, sulfamide, p-toluenesulphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamide, and mixtures thereof.

6. A process according to claim 1 wherein said adjunct ingredient admixed in step (iii) is selected from the group consisting of surfactants, buffers, chelants, abrasives, perfumes, colorants, dyes, bleach stabilizers, pigments, color speckles, suds suppressors, anti-tarnish agents, anti-corrosion agents, soil suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal agents, polymeric dispersing agents, thickeners, and mixtures thereof.

7. A process according to claim 6 wherein said adjunct ingredients are admixed with said bleaching composition after step (iv).

8. A process according to claim 1 wherein said source of hypochlorite is present in a ratio to said source of bromide from about 1:0.1 to about 1:2.

9. A process according to claim 8 wherein said ratio of hypochlorite to bromide is from about 1:0.2 to about 1:1.

10. A process according to claim 1 wherein said source of hypochlorite is present in a ratio to said  $\text{—NH}_2$  compound from about 10:1 to about 1:10.

11. A process according to claim 10 wherein said ratio of hypochlorite to  $\text{—NH}_2$  compound is from about 5:1 to about 1:2.

6,015,782

**13**

12. A process according to claim 11 wherein said ratio of hypochlorite to  $\text{—NH}_2$  compound is from about 3:1 to about 1:2.

13. A process according to claim 1 wherein said bleaching compound obtained from step (iv) from about 0.01% to about 10% available chlorine.

14. A process according to claim 13 wherein said bleaching compound obtained from step (iv) from about 0.01% to about 5% available chlorine.

15. A process according to claim 14 wherein said bleaching compound obtained from step (iv) from about 0.1% to about 2.5% available chlorine.

16. A process according to claim 15 wherein said bleaching compound obtained from step (iv) from about 0.5% to about 2.5% available chlorine.

17. A process according to claim 1 further comprising the step of adding a carrier to the pre-mix formed in step (i).

18. A process according to claim 17 wherein said carrier is water.

19. A process for manufacturing a liquid bleaching composition, said process comprising the steps of:

- i) mixing an aqueous solution of NaOCl wherein said NaOCl solution comprises from about 0.01% to about 10% available chlorine and NaBr to form a pre-mix; and
- ii) mixing an  $\text{—NH}_2$  compound selected from the group consisting of sulphamic acid, sodium sulphamate,

**14**

potassium sulphamate, sulfamide, p-toluenesulphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamide, and mixtures thereof with said pre-mix from step (i) to form a bleaching composition;

wherein the pH of said bleaching composition is greater than 12.

20. A process for manufacturing a liquid bleaching composition, said process comprising the steps of:

- i) mixing an aqueous solution of NaOCl wherein said NaOCl solution comprises from about 0.01% to about 10% available chlorine and NaBr to form a pre-mix;
- ii) admixing an  $\text{—NH}_2$  compound selected from the group consisting of sulphamic acid, sodium sulphamate, potassium sulphamate, sulfamide, p-toluenesulphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamide, and mixtures thereof with a surfactant to form a surfactant containing  $\text{—NH}_2$  admixture; and
- iii) mixing said surfactant containing  $\text{—NH}_2$  admixture from step (ii) to form a bleaching composition;

wherein the pH of said bleaching composition is greater than 11.

\* \* \* \* \*

## **EXHIBIT C**



US006037318A

**United States Patent** [19]

Na et al.

[11] **Patent Number:** 6,037,318[45] **Date of Patent:** Mar. 14, 2000

[54] **PROCESS FOR MANUFACTURING BLEACHING COMPOSITIONS COMPRISING CHLORINE AND BROMINE SOURCES AND PRODUCT THEREOF**

[75] **Inventors:** Henry Cheng Na; Michael Charles Frazee; James Charles Theophile Roger Burckett St. Laurent, all of Cincinnati; Kyle David Jones, West Chester, all of Ohio; Marco Petri, Angera Varese, Italy

[73] **Assignee:** The Procter & Gamble Company, Cincinnati, Ohio

[21] **Appl. No.:** 09/180,711

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§ 371 Date: Nov. 13, 1998

§ 102(e) Date: Nov. 13, 1998

[87] **PCT Pub. No.:** WO97/43392

PCT Pub. Date: Nov. 20, 1997

[51] **Int. Cl.<sup>7</sup>** ..... C11D 3/395; C11D 3/48; C11D 9/42

[52] **U.S. Cl.** ..... 510/379; 510/370; 510/380; 510/405; 510/499

[58] **Field of Search** ..... 510/367, 370, 510/379, 380, 405, 499

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*Primary Examiner*—Mark Kopeck

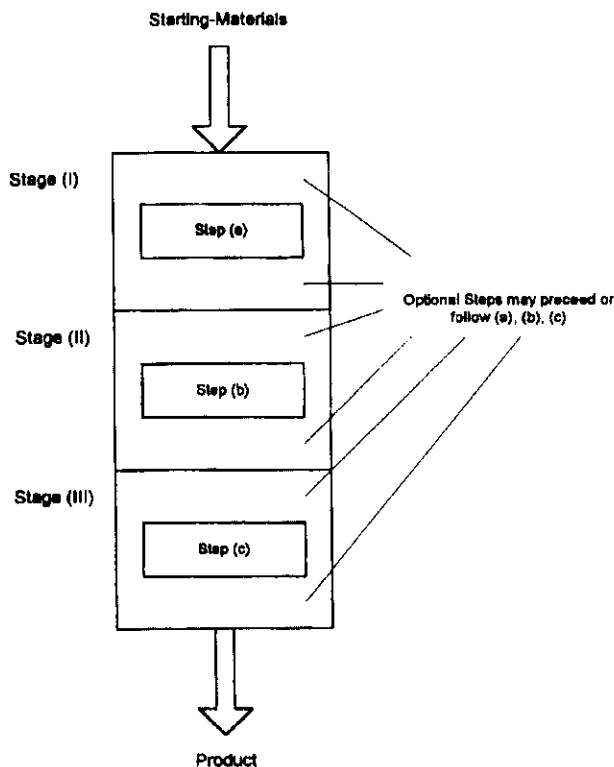
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[57] **ABSTRACT**

An improved process for the manufacture of alkaline bleaching compositions, especially liquid and/or gel compositions of high solubility and low abrasiveness, useful to the consumer, especially as products for hard surface cleaning, bleaching or disinfectancy. The products are made by a three-stage process and comprise particular chlorine and bromine bleach sources and particular aminofunctional materials such as low-impurity sulfamate. The process has mixing sequences and starting ingredient selections which provide unexpectedly improved product

**20 Claims, 1 Drawing Sheet**



U.S. Patent

Mar. 14, 2000

6,037,318

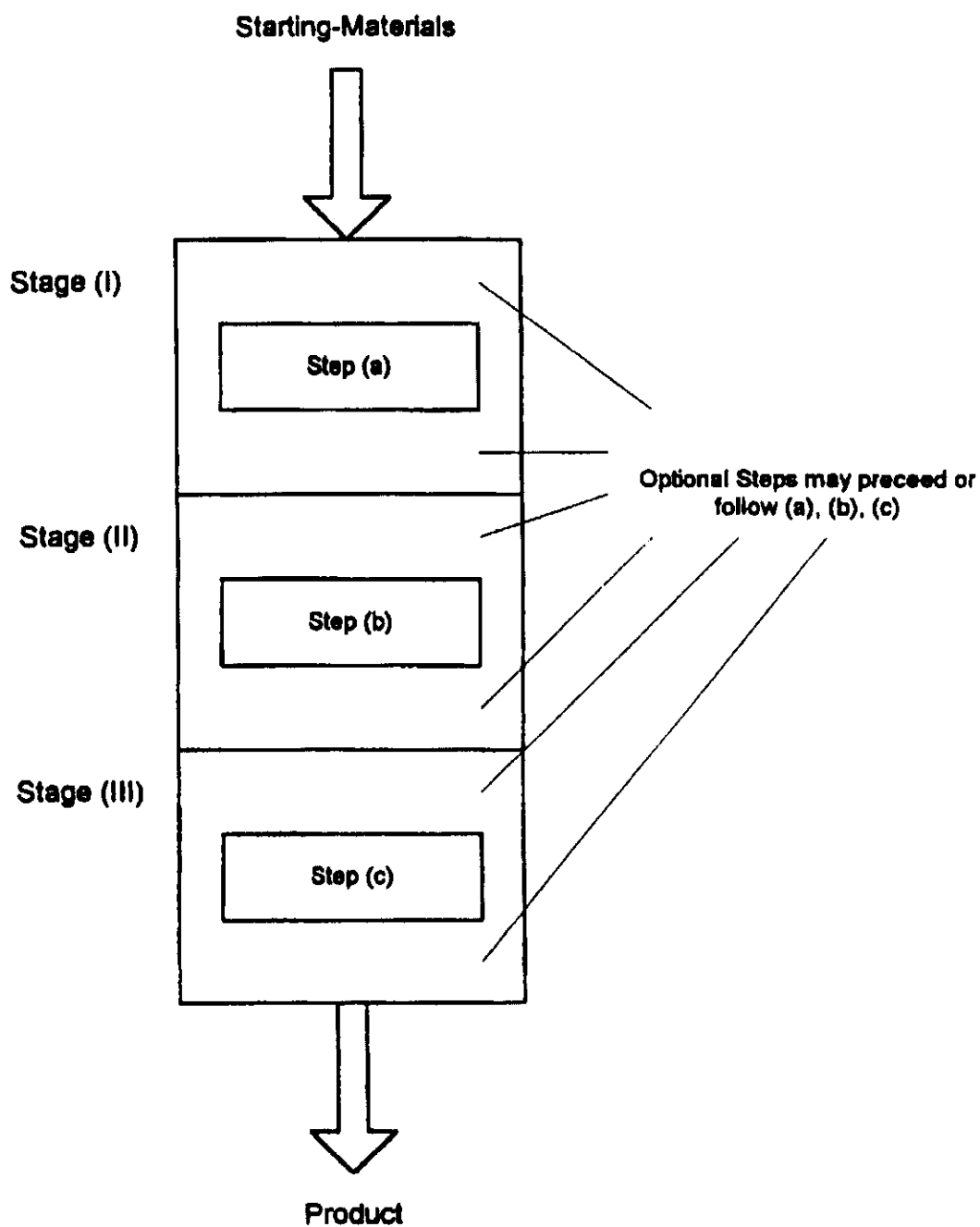


Fig. 1

6,037,318

1

# PROCESS FOR MANUFACTURING BLEACHING COMPOSITIONS COMPRISING CHLORINE AND BROMINE SOURCES AND PRODUCT THEREOF

## FIELD OF THE INVENTION

The present invention relates to a process for the manufacture of alkaline bleaching compositions useful to the consumer, especially as products for hard surface cleaning, bleaching or disinfectancy. The products comprise both chlorine and bromine bleach sources. The process has mixing sequences and starting ingredient selections which provide unexpectedly improved product.

## BACKGROUND OF THE INVENTION

Hard surface cleaners, bleaches and disinfectants are well known formulated consumer products. They are useful for treating all manner of soiled kitchen, bathroom, sink, tub, shower, toilet bowl and counter top surfaces.

Such consumer products are known to include hypochlorite bleach. Hypochlorite is desirable for its high effectiveness as a bleach and disinfectant. However, it has several disadvantages, including that it can sometimes be too aggressive, tends to leave an unpleasant odor on the hands, and is not always stable on storage in a consumer product formulation.

Bromine containing compounds have been used in specialized circumstances for bleaching or disinfectancy. However they tend to be expensive and are often even more demanding in terms of storage stability than the chlorine analogs.

Sulfamic acid has been used as a cleaner, especially in acidic cleaners delivering high concentrations of the acid.

The chemistry of sulfamate-containing systems with halogens is extraordinarily complex and research in this area continues to this day.

Despite the partly known features of the art, there is an ongoing need for hard surface cleaners, bleaches and disinfectants suitable for consumer use which are improved in one or more of their characteristics including having superior effectiveness as a bleach and disinfectant, being less aggressive, tending to leave very low odor or even pleasant odor on the hands, and being highly stable on storage.

Accordingly, an improved process for making such compositions is provided herein, and the alkaline bleaching compositions secured thereby.

The process herein has several advantages, including that it is easy to operate and is safe and effective for its intended purpose. Surprisingly, it delivers a product which is actually superior to the product which is achieved when numerous other mixing sequences are employed.

## BACKGROUND ART

Commonly assigned U.S. Pat. No. 3,583,922, Mc Clain and Meyer, Jun. 8, 1971 and Canadian Patent Publ. CA 860279 A, published Jan. 5, 1971 describe a solid composition for rapid removal of tannic acid stains having pH not less than 10.5 consisting of 0-95% abrasive, up to 10% surfactant, 0-60% alkaline builder, a stable compound, preferably chlorinated trisodium orthophosphate, to provide 0.5%-5% available chlorine, sulfamic acid to produce preferably a ratio of Cl to sulphamic add of 500 to 1:1, preferably 3:1 to 6:1, optionally with additives. Such additives can include bromides, perfumes or borax. The compositions can be adjusted for sink cleaning or mechanical dish washing.

2

JP 63108099 A, Lion Corp., published May 12, 1988 describes a bleaching agent for controlling chlorine odor containing a specific ratio of hypochlorite and sulfamic acid and/or sulfamate and pH adjusting agents. The ratio is 2-8 wt% hypochlorite based on "the amount of the effective chlorine" (sic) and there is a 0.25 to 1.5 mol ratio of sulfamic acid, and/or a sulfamate, to hypochlorite.

JP 63161088 A, Lion Corp., published Jul. 4, 1988 describes bleaching compositions for cloth comprising mainly hydrogen peroxide and sulfamic acid and/or water-soluble sulfamate and hypohalous acid and/or a water-soluble hypohalite salt such as NaClO, Ca(OCl)<sub>2</sub>, bleaching powder or NaBrO, the sulfamate being present in an amount of 0.5-5 mol per mol hypohalite.

U.S. Pat. No. 4,992,209, Feb. 12, 1991, Smyk et al describes a bactericidal, fungicidal system having a nitrite-containing corrosion inhibitor, for example cooling systems, prepared by reacting NaBr with NaOCl or Cl<sub>2</sub> and sodium sulfamate or sulfamic acid and the product is assertedly "reacted within 5 hours of preparation".

U.S. 5,431,839, Guillou, Jul. 11, 1995 describes sulfamic acid cleaning/stripping compositions comprising heteropolysaccharide thickening agents. U.S. Pat. No. 5,047,164, Sep. 10, 1991, Corby, describes compositions containing interhalogens and acid especially adapted for cleaning and disinfecting milk- and food-handling equipment. U.S. Pat. No. 4,279,764, Brubaker, Jul. 21, 1981 describes encapsulated bleaches comprising storage stable chlorinated isocyanurates. U.S. Pat. No. 4,233,173, Mayer et al, Nov. 11, 1980 and U.S. Pat. No. 4,201,687, Crutchfield et al describe detergent compositions containing chloroimidodisulfate bleaching agent. U.S. Pat. No. 5,470,499, Choy et al, Nov. 28, 1995 describes thickened aqueous abrasive cleansers with improved rinsability. Commonly assigned U.S. Pat. No. 4,051,056, Sep. 27, 1977, Hartman describes abrasive scouring compositions with perlite and hypochlorite bleach. Commonly assigned U.S. Pat. No. 3,715,314, Morgenstern, Feb. 6, 1973 describes scouring cleanser compositions. Commonly assigned U.S. Pat. No. 5,384,061, Wise, Jan. 24, 1995 describes stable thickened aqueous bleaching compositions comprising chlorine bleach and phytic acid. Industrial uses of sulfamic acid are included in a literature review, see "Inorganic Sulfur Chemistry", G. Nickless, Ed., Elsevier, 1968, Chapter 18, "Amido- and Imido-sulphonic acids", 607-667 and references cited therein; see also Kirk Othmer Encyclopedia of Chemical Technology, 3rd Ed., Wiley-Interscience, Vol. 21, "Sulfamic Acid and Sulfamates", pp 949-960. Chloramines, Bromamines and N-halamines more generally are reviewed in Kirk Othmer's Encyclopedia of Chemical Technology, Wiley-Interscience, 4th Ed., Vol. 5, pp 911-932; see also a corresponding article in the 3rd edition of the same Encyclopedia. Chlorine gas has previously been mixed with solutions containing sulfamic acid: see Korshak et al., Zh. Obsch. Khim., Vol. 18 (1948), pages 753-756, but the mixture decomposed.

## SUMMARY OF THE INVENTION

The present invention encompasses a process for manufacturing an alkaline bleaching composition, preferably an aqueous liquid bleaching composition, said process comprising at least three stages. These stages include, in sequence (I) a pre-bromine stage, (II) a bromine compound addition stage, and (III) a product stabilization stage, and each of said stages has at least one mixing step.

In said process, said pre-bromine stage, (I), comprises a step, (a), of mixing in any order components comprising a

6,037,318

3

hypochlorite source and an aminofunctional compound having a stable N-halo derivative; thereby forming a stage (I) mixture; provided that at the end of said pre-bromine stage, said stage (I) mixture has a pH not exceeding about 11, preferably lower; said bromine compound addition stage, (II), is initiated at said pH and comprises a step, (b), of mixing in any order with said stage (I) mixture, a bromine compound; thereby forming a stage (II) mixture; and said product stabilization stage, (III), comprises at least one step, (c), of mixing in any order with said stage (II) mixture, an alkali in an amount suitable to arrive at a final pH for the product of said process of at least about 13.

The product provided by this process has unique advantages in terms of excellent bleaching effect at the same time as permitting a minimization of "bleach odor" on skin. The preferred product is a transparent yellow aqueous liquid, which may optionally be thickened and/or perfumed.

All percentages, ratios, and proportions herein are on a weight basis unless otherwise indicated. All documents cited are hereby incorporated by reference in their entirety.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 represents a schematic outline of the present process, showing the conversion of starting-materials (ingredients) to product via a series of stages, comprising, in sequence, Stage (I), Stage (II) and Stage (III). Each stage, as indicated, includes one or more steps. Stage (I) includes an essential step, namely Step (a). Stage (II) includes an essential step, namely Step (b), and Stage (III) includes an essential Step, namely step (c). The present process in the most reduced form which can be constructed from FIG. 1 consists of the sequence of three steps (a) followed by (b) followed by (c). Each of the essential stages and steps, as well as suitable ingredients and characteristics of the product are described in detail hereinafter.

#### DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been discovered that in order to secure an alkaline bleaching composition having superior technical performance and desirability for the consumer, it is necessary to provide two distinct types of halogen ingredient including at least one having, at the outset, the form of a bromine compound and at least one having, at the outset, the form of a hypophalite compound. It has also been found essential to particularly select and include a certain aminofunctional compound; and to provide a particular process, especially in terms of mixing sequence, to secure the product benefits.

##### Alkaline Bleaching Compositions

Accordingly, the present invention relates to processes for making alkaline bleaching compositions and to the products thereof. "Alkaline bleaching compositions" as defined herein are strongly alkaline. The "alkaline bleaching compositions" herein have a pH as is of at least about 13, and are made from ingredients comprising a hypophalite source and a bromine compound along with at least one particularly selected aminofunctional compound. Alkaline bleaching compositions herein are useful to the consumer as products for hard surface cleaning, bleaching or disinfectancy. They can, in general, have any suitable physical form, such as granular, tablet, paste, gel or liquid form, and can be aqueous or non-aqueous. However, the process herein is especially well adapted for making aqueous, alkaline, liquid-form or gel-form bleaching compositions; technical problems of processing are greatest for such compositions. Unless oth-

4

erwise noted, embodiments hereinafter which illustrate the processes and product of the invention therefore relate to the aqueous liquid forms.

##### Process Stages

Processes herein generally comprise at least three stages:

- (I) a pre-bromine stage;
- (II) a bromine compound addition stage, and
- (III) a product stabilization stage.

The stages are carried out in the order (I) then (II) then (III). The stages are identified in FIG. 1. Each stage includes one or more steps. In a minimum configuration, the process includes, in Stage (I), step (a); in Stage (II), step (b), and in Stage (III), step (c). Additional steps, for example of adding and/or mixing other ingredients such as perfumes, surfactants and the like, may be inserted before or after any of the essential steps, provided that they do not affect the indicated sequence of essential steps and further, that they are performed compatibly with respecting the pH criticalities described herein.

In more detail, Stage (I), the pre-bromine addition stage, is a stage used to bring together a hypochlorite source and a particular aminofunctional compound; Stage (II), the bromine compound addition stage, is a stage used to introduce a bromine compound; and stage (III), the product stabilization stage, is a stage used to stabilize the product by increasing pH.

Thus the invention encompasses a process for manufacturing an alkaline bleaching composition, said process comprising at least three stages including, in sequence, (I) a pre-bromine stage, (II) a bromine compound addition stage, and (III) a product stabilization stage, each of said stages having at least one mixing step; wherein in said process, said pre-bromine stage comprises a step, (a), of mixing in any order components comprising a hypochlorite source and an aminofunctional compound having a stable N-halo derivative; thereby forming a stage (I) mixture; provided that at the end of said pre-bromine stage, said stage (I) mixture has a pH not exceeding about 11; said bromine compound addition stage is initiated at said pH and comprises a step, (b), of mixing in any order with said stage (I) mixture, a bromine compound; thereby forming a stage (II) mixture; and said product stabilization stage comprises at least one step, (c), of mixing in any order with said stage (II) mixture, an alkali in an amount suitable to arrive at a final pH for the product of said process of at least about 13.

Particularly preferred processes herein are restrictive in terms of when the bromine compound may be added. In preferred processes, no stage other than (II) and no step other than (b) comprises adding a bromine compound. Surprisingly, it has been found that adding bromine compound elsewhere in the sequence has a negative impact on product performance.

##### Optional Process Steps

The present process can include various optional steps. An optional step useful herein is illustrated by a dilution step, included in the process after completion of stage (III). Such a step as a dilution step can in fact be carried out either by the manufacturer, or by the user of the product of stages (I), (II) and (III). Dilution steps can in general be included in stage (I), stage (II) or stage (III) of the present process, though preferably, dilution is avoided in those stages. Typically for best storage stability, a dilution step is not carried out in the plant, but rather, by the consumer who uses the composition. Dilution can result in pH variation, typically including pH decrease. Other optional steps useful herein include surfactant addition steps, or steps of adding or mixing any suitable optional ingredient, such as those identified under "optional ingredients" hereinafter.



6,037,318

5

### Process Means

Any suitable means may be employed for accomplishing the present process. Reactors are desirably chemically inert to halogen bleach and strongly alkaline conditions, plastics and/or borosilicate glass lined apparatus is desirably used both for durability and to minimize contamination of the product by metals. Reactors need not be designed for operation under pressure provided that suitable venting is provided. Mixing of ingredients can be accomplished using any suitable mixer, such as a motor-driven paddle. Alternately, a centrifugal pump can be used to provide a recirculating jet of product solution, driving agitation of the mixture. Other useful process means herein include means for removing vapors from the work environment. Such means include conventional scrubbers, etc.

### Process Conditions

#### Temperature

In general the present process can be carried out at widely ranging temperatures. Preferably, each of said steps (b) and (c) is performed at a temperature in the range from about 5° C. to about 80° C., preferably from about 10° C. to about 45° C., most preferably at or about ambient temperature, e.g., about 20° C. Highly preferred process herein accomplish all steps in stages (I), (II) and (III) at such temperatures. At higher temperatures, there may be an increased decomposition tendency and at lower temperatures, freezing can be a problem.

#### pH's

The present process requires particular limits on pH variation. There is a general requirement that at the end of the pre-bromine stage and at the beginning of the bromine stage, the pH of the stage (I) mixture is not in excess of about 11. In preferred embodiments, this pH is not in excess of about 8, more preferably, it lies in the range from about 1 to about 6.9.

In preferred embodiments, from the end of stage I, the entire process is conducted at a rising pH. Such rising pH desirably corresponds with a value of  $dpH/dt$  of at least about +0.1 pH units/min, preferably about +0.5 pH units/min, or higher.

In such embodiments, it will be appreciated that the instant process contains a pH minimum. The position in the overall sequence of the present process of this minimum is found at the end of stage (I).

#### Pressure

The present process can be conducted at any convenient pressure. For example, chlorine gas and alkali can be reacted under pressure, for example up to about 5 atm., in stage (I) prior to adding the aminofunctional compound; and the following stages of the process can be conducted at atmospheric pressure, or even at reduced pressure if scrubbers or condensers are provided for collecting lost halogen. Preferred processes are conducted at atmospheric pressure.

#### Time

The present process can be conducted in batch or continuous mode. Unless otherwise indicated, illustrations of the process hereinafter are batch-mode. Times for completion of a batch may in general vary widely. Typically, times of about 5 min to about 1.5 hours are typical for each of stages (I), (II) and (III). In preferred embodiments, Stage (II) will allow at least sufficient time to permit the bromine compound to substantially dissolve before proceeding with stage (III). Also preferably, stage (II) is continued until development of a yellow color in the stage (II) mixture. In general, the longer process times are associated with larger-scale processes. It is preferred herein to minimize the overall reaction time, and in particular, while allowing sufficient

6

time for stage (II), to proceed without delay from that stage to the end of stage (III). Moreover, it is highly preferred to minimize any time period between the end of step (a) and the beginning of step (b), and between the end of step (b) and the beginning of step (c).

### Concentration and Concentration Ratios

The present process can be conducted over a wide range of concentrations of the ingredients in water. In preferred embodiments, the process is characterized by a dilution factor for the sum of stages subsequent to stage (I) which is not in excess of about twofold. In general, concentrations of the ingredients are adjusted such that the product of stage (III), comprises from about 0.01% to about 10% Available Chlorine. Also, in terms of relative proportions of the ingredients, the present process preferably relies on an interhalogen ratio  $[Br] : [OCl^-]$  of from about 10: 1 to about 1: 10, preferably 1:2 to 1:5, wherein  $[Br]$  represents total moles Br added into said process from said bromine compound and  $[OCl^-]$  represents total moles hypochlorite added into said process from said hypochlorite source. Moreover, the preferred processes herein employ an amino-halo ratio  $[A] : [X]$  of from about 10: 1 to about 1: 10, wherein  $[A]$  represents the total of moles of amino moieties of said aminofunctional compound used to form said composition and wherein  $[X]$  represents total moles of bleaching halogen, measurable as Available Chlorine, added into said composition.

Very preferably, said amino-halo ratio is from about 1.0: 1.0 to about 1.5: 1.0.

To illustrate, with respect to the above quantities, sulfamic acid, which contains one mole of amino moieties per mole of the compound, is easily computed in the above relation:  $[A]$  is simply the number of moles of sulfamate; but to give another illustration, when melamine is used,  $[A]$  is the number of moles of melamine used multiplied by the number of moles (which is 3) of amino moieties contained in any one mole of melamine.

### Ingredients

#### Hypochlorite Source

In general, any convenient hypochlorite source can be used in the instant process. Preferred hypochlorite sources are selected from chlorine, hypochlorous acid, alkali metal hypochlorites, alkaline earth metal hypochlorites, the product of mixing a hypochlorite-liberating compound with aqueous alkali, and mixtures thereof. Suitable hypochlorite-liberating compounds, in the sense immediately above, are illustrated by dichloroisocyanuric acid and its sodium salts and hydrates, which hydrolyze rather readily to release hypochlorite. Highly preferred hypochlorite sources herein are selected from alkali metal hypochlorites and the product of mixing said hypochlorite-liberating compound and aqueous alkali.

#### Aminofunctional compound

From the thousands of available aminofunctional compounds, the present invention selects a limited few which are found operative. In processes of the invention, suitable aminofunctional compounds are those having stable N-halo derivatives. The term "having a stable N-halo derivative" herein is defined as "capable of forming an N-halo derivative and it is stable", rather than as necessarily "possessing a stable N-halo moiety at the inception of the present process". Suitable aminofunctional compounds meeting the needs of the present invention are selected from (i) primary aminofunctional compounds selected from sulfamic acid, alkali-metal sulfamates, alkaline earth sulfamates, tetra-alkylammonium sulfamates, and mixtures thereof; (ii) secondary aminofunctional compounds selected from second-

6,037,318

7

ary amine derivatives having formula  $RR'NH$  or  $(R'')_2NH$  wherein  $R$ ,  $R'$  and  $R''$  are organic moieties and wherein carbon atoms of said organic moieties are bonded covalently to  $NH$ ; (iii) sulfonamides selected from sulfamide, p-toluenesulfonamide, imidodisulfonamide, benzenesulfonamide, alkyl sulfonamides, and mixtures thereof; (iv) melamine, cyanamide; and (v) mixtures thereof.

Suitable secondary aminofunctional compounds (ii) include those not specifically identified in (i), (iii), (iv) and (v), wherein  $R$ ,  $R'$  and  $R''$  are independently selected from C1-C12 linear saturated and C3-12 branched saturated moieties which can be alkyl, aryl or heterocyclic, optionally substituted by carboxylic acid or carboxylate; an example of the latter carboxylic-substituted derivatives is the alpha-aminobutyrate. Preferred secondary aminofunctional compounds are known for use as disinfectants, especially those which are water-soluble and those having N-halo derivatives which are relatively insensitive to shock.

In alternate terms, the present process is believed to be applicable wherever the aminofunctional compound has a hydrolysis constant,  $K$ , as defined by

$$K = [HOCl][RNH_2] / [RNHCl]$$

$$\text{or } K = [HOCl][RR'NH] / [RR'NCl]$$

$$\text{or } K = [HOCl][(R'')_2NH] / [(R'')_2NCl]$$

in the range of from about  $10^{-6}$  to about  $10^{-9}$ , provided that no isocyanurate or chlorinated isocyanurate is included as the essential aminofunctional compound.

Hydrolysis constants such as the above are well known in the art and are defined conventionally. See, for example, Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 5, article entitled "Chloramines and Bromamines", see especially page 567, and Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 3, see especially pages 940-941, these articles being incorporated herein by reference.

Subject to the above-identified requirements, preferred secondary aminofunctional compounds can be selected from those identified in Kirk Othmer, Encyclopedia of Chemical Technology, 4th. Ed., 1993, pages 918-925 and include compounds identified under the headings "Organic Chloramines and Bromamines", "Aliphatic Compounds", "Aromatic Compounds" and "Heterocyclic Compounds".

Sulfamic acid or sodium sulfamate are highly preferred aminofunctional compounds herein.

#### Alkali

Suitable alkali in the present process is selected from alkali-metal-, alkaline-earth-, and tetraalkylammonium-oxides, hydroxides, carbonates, bicarbonates, silicates, phosphates, borates, and mixtures thereof.

#### Bromine compound

Suitable bromine compounds in the present process are selected from the group consisting of bromine, water-soluble bromide salts, water-soluble hypobromite salts, hypobromous acid, and mixtures thereof.

#### Overall Preferred Combinations of Ingredients

In an overall preferred process herein, said hypochlorite source is selected from alkali metal hypochlorites and the product of mixing a hypochlorite-liberating compound and aqueous alkali; said aminofunctional compound is selected from sulfamic acid, alkali-metal sulfamates, alkaline earth sulfamates, tetra-alkylammonium sulfamates, and mixtures thereof; and said bromine compound is selected from the group consisting of water-soluble bromide salts. Highly preferred herein is a process wherein said hypochlorite

8

source is sodium hypochlorite, said aminofunctional compound is sulfamic acid; and said bromine compound is selected from sodium bromide, potassium bromide and mixtures thereof.

#### Ingredients or Impurities Desirably Excluded

The present process and product thereof preferably limits certain compounds which have been found to adversely affect product stability and effectiveness. Especially undesirable compounds herein are those aminofunctional compounds which do not form stable N-halo derivatives. Such compounds include simple ammonium ( $NH_4^+$ ) salts, such as ammonium sulfate; urea; amino acids such as aspartic acid; and mixtures thereof, any of which may, for example, produce unpleasant odors of undesirable chloramines. Preferred herein are processes wherein throughout, and at least in the essential aminofunctional compound, no ingredient comprises more than about 1% of aminofunctional impurity compounds having unstable N-halo derivatives. Translating this requirement in practical terms, sulfamic acid is commercially available in a range of grades, certain of which may include urea as an impurity.

The crystal grade of sulfamic acid, which minimizes urea impurity, is found to be preferred. In other process embodiments, the present process is conducted using starting materials which are all water-soluble that is to say, excluding insoluble materials such as abrasives, thereby avoiding any tendency for surface-catalyzed bleach decomposition.

#### Acids and Bases for pH Adjustment

Any convenient alkali or base can be used herein as a pH-adjusting agent for increasing pH, and any convenient acid can be used herein as a pH-adjusting agent for decreasing pH; always provided that such alkali or acid is non-reactive with hypochlorite. Preferred alkalis for pH adjustment include water-soluble alkalis such as sodium hydroxide, potassium hydroxide or mixtures thereof, and preferred acids include the common mineral acids such as sulfuric, hydrochloric or nitric, though sulfuric is preferred in this group. Alternately relatively weak acids can be used; these include acetic acid.

Examples of bases which knowledgeable practitioners will avoid entirely in the present process include ammonia because it is chemically reactive with other essential ingredients herein for purposes other than pH change, forming, for example, an undesirable type of chloramine when it reacts with hypochlorite.

In general, any simple mineral acid or base additions in the present process will be carried out in a manner consistent with preserving the chemical integrity of the aminofunctional compound. For example, when using sulfamic acid as the aminofunctional compound, mineral acid additions are conducted under sufficient dilution to avoid decomposition of the sulfamic acid. Concentrated nitric acid, for example, is known to decompose sulfamic acid at  $HNO_3$  concentrations of 73%, especially at elevated temperatures, with formation of nitrous oxide, and such combination of concentrated mineral acid and elevated temperature is avoided in the instant process.

#### Water

Water used for making liquid compositions according to the present process is suitably city water. In general, hard, soft, softened or deionized water may be used. Distilled or reverse-osmosis treated water are especially desirable. When using water of uncertain quality, for example ferruginous water or high-manganese water from boreholes, it is desirable to reduce the dissolved metal content by conventional water treatment approaches, for example,

6,037,318

9

oxygenation, filtration, and settling. Moreover a chelant or sequestrant can be used to treat process water. It is prudent to monitor or periodically check, and if needed, minimize transition metal ion content of the water by conventional techniques since transition metal ions are well known to affect bleach product stability. Suitable analysis is by atomic absorption spectroscopy or inductively coupled plasma spectroscopy (ICP).

#### pH Measurement

pH herein is measured using a glass electrode or combination electrode such as Coming General Purpose Combination electrode Cat. No. 476530, and a commercial pH meter such as the  $\Phi$  40 pH meter available from Beckman.

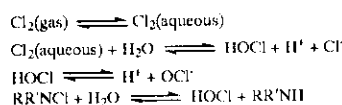
#### pH Ramping

It is desirable, and indeed characteristic of the present process as best currently known, for there to be present a downward pH ramp (a "ramp" herein being a relatively linear increase or decrease in pH with time) followed by an upward pH ramp, there being a strong minimum in the pH as indicated in the process definition. In the latter part of the process, as noted hereinabove, the upward ramp of pH, measurable by dpH/dt, is specifically in a defined range believed to be linked to stability and performance.

#### Bleach ingredient measurement: Available Chlorine

The term "Available Chlorine" sometimes abbreviated "AvCl<sub>2</sub>" as used herein is described in Kirk Othmer's Encyclopedia of Chemical Technology, Vol. 4, 4th Ed. (1992) pages 274-275 published by Wiley-Interscience.

Reactions which produce an oxidant from chlorine include the following:



The total concentration or amount of any given chlorine-based oxidant is often pressed on an equivalent basis, as though all the oxidant were chlorine. Available Chlorine is thus the equivalent concentration or amount of chlorine needed to produce an oxidant, for example according to the above reactions, and can be measured by conventional measures, such as iodometric methods referenced in Kirk-Othmer (op. cit).

Available Chlorine can be calculated from the following relation:

$$\text{Available Chlorine (\%)} = 71.9 \times \frac{\text{moles of oxidant} \times (\text{number of active Cl atoms / molecule}) \times 100}{\text{moles of oxidant}}$$

In the above relation, the term "active Cl atoms" needs definition: Because Cl<sub>2</sub> only accepts two electrons, as does HOCl and monochloroamines, it has only one "active" Cl atom according to the present definition.

When determining the Available Chlorine expected for product of the instant process, "moles of oxidant" in the above relation is replaced by "total moles of bleaching halogen added in forming the composition".

Note that "Available Chlorine" can be determined for bleaches that do not actually form hypochlorite in solution, such as bromine-containing bleaches, and other nonchlorine bleaches, by substituting the number of electrons accepted divided by two for the number of active chlorine atoms in the above relation. This can also be measured by iodometric titration.

Note also that the Available Chlorine unit is a dimensionless percentage, not a percentage by weight. It should be

10

apparent from the definition that it is in fact possible in general terms to obtain Available Chlorine values which exceed 100%; this can happen in the case of a chlorine bleach which is more mass efficient than Cl<sub>2</sub>, recalling that only one chlorine atom in Cl<sub>2</sub> is a bleaching chlorine atom; however, such levels are not encountered in the present process.

#### Amounts and Ratios of ingredients

In general, amounts and aqueous concentrations of ingredients herein may vary quite widely; nonetheless there is a strong preference for particular interhaogen ratios as defined elsewhere herein and it is commercially attractive to use ingredients such as sodium hypochlorite at the most economic concentrations provided by their manufacturers.

#### Advantages

As noted, the present invention has significant advantages, for example improved bleaching. By "improved bleaching" it is meant herein that a composition obtainable with the process of the present invention delivers better bleaching performance on bleachable stains like tea stains, as compared to the bleaching performance delivered by the same composition made by another process, for example one involving numerous alternate orders of addition or mixing of the ingredients. Importantly, concurrent with improved bleaching, the formulations provided by the process leave low residual odor on skin and are milder than those otherwise manufactured with different ingredient selections and/or orders of addition. In short the combination of overall performance and desirable skin safety/laesthetics offered by the present process are believed to be measurably superior to those attainable by any art-recognized process.

#### Product Characteristics

The product of the present process is not in general limited as to form, though it is highly preferred for the compositions produced to be aqueous liquids or aqueous gels. Another product form potentially preferred herein is a "high-solubility solid concentrate" or "high solubility tablet" form. Such product forms are free from abrasives. The product of the process is preferably transparent, and, as described elsewhere herein, may be both colored and perfumed.

#### Processing of Optional Ingredients

The present process and the product thereof allow for the presence of at least one additional mixing step other than the essential minimum (a), (b), (c); wherein there is added an ingredient selected from the group consisting of surfactants, buffers, builders, chelants, perfumes, colorants, dyes, bleach stabilizers, pigments, suds suppressors, anti-tamish and/or anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removavanti-redeposition agents, thickeners, solvents, and mixtures thereof. For other optional ingredients, see U.S. Pat. No. 3,583,922 or other references cited in the background, recognizing that '922 relates to solid compositions as distinct from the liquids herein.

#### Other Ramifications

The present process can accomodate perfumes and colorants, most particularly known bleach-stable colorants such as various yellows; and perfumes offering citrus or pine character. Perfumes for use herein are desirably hydrophobic, having relatively high octanol/water partition coefficients such as 6 or above. In process terms, it has been found desirable to incorporate perfume in a step which follows (III) (a). Without being limited by theory, this is believed to be due to a reduced tendency for reaction of sulfamate derivatives with perfume aldehydes when they are



6,037,318

11

incorporated late in the process. Also desirably, bleach-stable thickeners such as those referenced in background and/or Laponite®, a special clay available from Laport, and/or fatty amine oxides may be combined using the present process to deliver product having a wide range of useful properties.

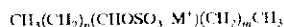
#### Optional Ingredients in More Detail

Optional ingredients are now nonlimitingly illustrated in more detail. Such ingredients as noted include surfactants, bleach stabilizers, colorants, suds boosters, suds suppressors, anti-tarnish and/or anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal/anti-redeposition agents, polymeric dispersing agents, and the like; and mixtures thereof.

The processes herein may make use of, based on the composition of the product, from about 0.1 % to about 95% of a surfactant or mixtures thereof selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic surface active agents. For liquid systems, surfactant is preferably present to the extent of from about 0.1 % to 20%, though higher levels, e.g., 30% are possible, for example in viscous gels, aqueous pastes or semi-solids.

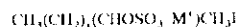
Anionic surfactants herein can include water-soluble salts, particularly the alkali metal salts, of  $C_8$ - $C_{22}$  organic sulfuric reaction products and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Sodium or potassium alkyl sulfates, especially those obtained by sulfating  $C_8$ - $C_{18}$  alcohols are useful, as are linear or branched alkyl benzene sulfonates especially the  $C_9$ - $C_{15}$  alkyl-substituted sodium- or potassium- salt forms; also useful are the sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil; and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, conventional primary alkyl sulfates, such as those having the general formula  $ROSO_3^-M^+$  wherein R is typically a linear  $C_8$ - $C_{22}$  hydrocarbon group and M is a water solubilizing cation are useful herein, as are the secondary alkyl sulfates and/or branched chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms, see EP 439,316 A Smith et al. Secondary alkyl sulfate surfactants include those materials which have the sulfate moiety distributed randomly along the hydrocarbon "backbone" of the molecule. Such materials may be depicted by the structure

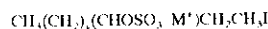


wherein m and n are integers of 2 or greater and the sum of m+n is typically about 9 to 17, and M is a water-solubilizing cation.

In addition, the selected secondary (2,3) alkyl sulfate surfactants used herein may comprise structures of formulas I and II



12



for the 2-sulfate and 3-sulfate, respectively. Mixtures of the 2- and 3-sulfate can be used herein. In formulas I and II, x and (y+1) are, respectively, integers of at least about 6, and can range from about 7 to about 20, preferably about 10 to about 16. M is a cation, such as an alkali metal, ammonium, alkanolammonium, triethanol-ammonium, potassium, ammonium, and the like, can also be used.

The aforementioned secondary alkyl sulfates are those prepared by the addition of  $H_2SO_4$  to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued Feb. 8, 1996 or in U.S. Pat. No. 5,075,041, Lutz, issued Dec. 24, 1991. The synthesis conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products which, when purified to remove the unreacted materials, randomly sulfated materials, unsulfated by-products such as C10 and higher alcohols, secondary olefin sulfonates, and the like, are typically 90+% pure mixtures of 2- and 3- sulfated materials (some sodium sulfate may be present) and are white, non tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5% of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available as under the name "DAN", e.g., "DAN 200" from Shell Oil Company.

Especially preferred surfactants for use in the present process are those having the highest possible bleach stability, including  $C_8$ - $C_{22}$  fatty amine oxides such as hexadecydimethylamine N- oxide or saturated fatty alkyl alkoxyates. Particularly objectionable surfactants are those having a high degree of unsaturation, and any surfactants comprising hypohalite-reactive nitrogen moieties. Somewhat less problematic, but still a potential source of difficulty, are the use of any alcohols. Thus, when using alkyl ethoxyates, etc., the so-called "capped" forms in which terminal  $-OH$  is replaced by  $-OCH_3$  or similarly unreactive groups, is particularly preferred.

The most bleach-stable and hydrolytically-stable surfactants can be added at various stages of the present process, but for convenience, their addition will generally be done in such manner as to minimize foaming which may undesirably slow down the process. Silicone anti-foams are desirable for limiting foam; such anti-foams are commercially available from Dow Corning Corp.

When processing a surfactant having susceptibility to acid hydrolysis, such as an alkyl sulfate, it is incorporated into the product in the present process at any point at which the pH of the mixture of ingredients has exceeded about 7, preferably, when said pH has exceeded about 8.

Although preferred processes and compositions herein are free from insoluble materials and are non-abrasive, products of the present process can be formulated in a solid or viscous semi-solid form further comprising an abrasive material, such as expanded perlite abrasive in combination with the surfactants, filler material, or other optional scouring material ingredients listed herein. When desired, abrasive materials can be those contained in U.S. Pat. No. 4,051,056, Hartman, issued Sep. 27, 1977.

Other optional ingredients to be used herein include buffers, for purposes which include to adjust the cleaning surface pH to optimize the hard surface cleaner composition effectiveness relative to a particular type of soil or stain. Buffers may also be included to stabilize the adjunct ingredients with respect to extended shelf life or for the purpose of maintaining compatibility between various aesthetic ingredients. The hard surface cleaner of the present invention optionally contains buffers to help adjust and maintain

6,037,318

13

the pH at about 13 or in a range above about 13. Non-limiting examples of such suitable buffers are potassium carbonate, sodium carbonate, and trisodium phosphate, however, the formulator is not restricted to these examples or combinations thereof.

The cleaning compositions obtainable according to the process of the present invention may also desirably be prepared with inclusion of a heavy metal ion control system, especially one comprising one or more agents for the control of bleach destabilization caused by soluble, insoluble or colloidal iron and/or manganese and/or copper. A simple but effective agent is sodium tripolyphosphate, optionally supported by at least partially polymeric hydrous sodium silicate. Examples of other chelating or heavy-metal control agents are phytic acid and ethane-1-hydroxy-1,1-diphosphonic acid (EHDP), though other materials, such as a number of commercial phosphonate types, may be used. Preferred chelating agents herein, are free from alcohol sites, halogen-reactive nitrogen donor sites, and hydrolically sensitive sites. In process terms, a preferred addition of at least some chelating agent or heavy-metal ion control agent takes place at or near the beginning of the process, for example immediately before, or concurrent with, step I(a). However, when adding a silicate for the purpose at least in part of helping control heavy metal ions, it is added at a point in the process which is remote from both the pH minimum and the pH maximum of the process.

Perfumes when used are typically at levels of from 0% to 5%. See U.S. Pat. No. 4,246,129, Kacher, issued Jan. 20, 1981.

The compositions obtainable according to the process of the present invention typically have a yellow color. However, it is possible to provide a preferred solution which has some other color, for example, by the addition of a bleach-stable dye; moreover, preferred solutions may readily be diluted, in which case yellow color is difficult to detect. In process terms, dyes are preferably added at the end of the process, in which case product-making can be more conveniently monitored on a colorant-free product.

The liquid compositions obtainable according to the process of the present invention may be formulated with different viscosities. In one embodiment of the present invention the compositions obtainable with the process herein have a viscosity of from about 1 to about 150 cps. Said compositions are convenient for spray bottle application. Likewise, said liquid compositions obtainable according to the present invention can be further thickened, e.g., by the addition of additional bleach-stable thickener, such as the commercially available DOWFAX. A suitable gel formulation has a viscosity of from about 100 cps to about 2000 cps, preferably from 300 cps to 1000 cps as measured, for example, by techniques and methods described in "Physico-Chemical Methods", Reilly, J. and Rae, W. N.; Vol. 1 (5th ed.), pages 667-692; D. Van Nostran pub. Thickeners, when added in the instant process, are desirably used toward the end of the process, for example, adding them immediately after, or concurrent with, stage (III).

#### EXAMPLE I

##### (I) Pre-Bromine Stage

All operations are conducted at ambient temperature, about 20° C. 30 grams distilled water is placed in a chemically inert, plastic-lined reaction vessel. The vessel is set for operation at atmospheric pressure and as a precaution is connected to a scrubber for removing any minor quantity of chlorine vapors which might be emitted. The vessel is equipped with an inert-plastic-coated paddle stirrer. While stirring at 300 rpm, 13.05 grams of aqueous sodium

14

hypochlorite, assayed as comprising 10.73% Available Chlorine, is added. Immediately thereafter, sulfamic acid (2.2 grams, Aldrich, 99.3%, crystalline) is added with continued stirring until the added solid has dissolved. At this point, the pH of the stage (I) mixture is about 1.0.

##### (II) Bromine Compound Addition Stage

To the stirred stage (I) mixture is added Sodium Bromide (0.5 grams, EM Science). The mixture is stirred until the added solid has dissolved (about 5 minutes) and a yellow color has appeared. The mixture at this point is identified as a Stage (II) mixture.

##### (III) Product Stabilization Stage

To the stirred stage (II) mixture is added Sodium Hydroxide (about 3.0 grams, 50% in water) until the pH of the mixture is about 13.2. Water is added until the total weight of the stage (III) mixture is about 100 grams.

#### EXAMPLE II

The process of Example I is repeated with the following differences: The scale of operations is increased 1000-fold. In a pre-processing step, chlorine gas is passed into sodium hydroxide solution, forming sodium hypochlorite solution. The sodium hypochlorite solution is passed into the above-identified reactor in batches, where it is treated with sulfamic acid, forming a stage (I) mixture. Steps subsequent to stage (I) are conducted in the manner of Example I.

#### EXAMPLE III

The process of Example II is repeated with the following difference: Sodium Sulfamate is substituted for sulfamic acid.

In the examples below, a heavy line indicates the boundary separating Stages (I), (II) and (III) of the process.

#### EXAMPLE IV

The process of Example III is repeated with the following difference: prior to completion of Stage I, aqueous hydrochloric acid is added to reduce the pH to about 7.0.

Ingredient	Addition Sequence	% wt
Hydrous Sodium Silicate (Britesil H2O, PQ Corp.)	(2)	0.20
Sodium Tripolyphosphate	(3)	0.20
First portion		
Sodium Hypochlorite	(4)	0.90
Sulfamic Acid	(5)	1.30
Potassium Bromide	(6)	1.10
Sodium Tripolyphosphate	(7)	7.60
Second Portion		
Sodium Hydroxide	(8)	0.80
Cocodimethylamine N-Oxide	(9)	0.25
Dye	(10)	0.15
Perfume	(11)	0.60
Water	(1) and (12)	bal.

("bal." means "balance to 100%")

Ingredient	Addition Sequence	% wt
Sodium Hypochlorite	(2)	1.4
Sulfamic Acid	(3)	1.9
Sodium Silicate	(4)	0.04
Sodium Bromide	(5)	1.8
Sodium Hydroxide	(6)	1.6

6,037,318

15

-continued

Ingredient	Addition Sequence	% wt
Surfactant	(7)	3.5
Dyes/perfume	(8)	0.28
Water	(1) and (9)	bal.

Note:

\*\*Surfactant" refers to C8 Alkyl Sulfate, C12-C14 Dimethylamine N-Oxide or a mixture thereof.

Ingredient	Addition Sequence	% wt
Sodium Hypochlorite	(1)	1.4
Sodium Sulfamate/ Sulfuric acid	(2)	2.2**
Sodium Bromide	(3)	1.5
Potassium Bromide	(4)	1.1
Sodium Silicate	(5)	0.05
Perfume	(6)	0.1
Sodium Hydroxide	(7)	1.8
Sodium Octyl Sulfate	(8)	5.5
Yellow Dye	(9)	0.28
Water	(10)	bal.

("bal." means "balance to 100%")

\*\*weight equivalent to sulfamic acid content, dry basis

Ingredient	Addition Sequence	wt %
Cocodimethylamine N-oxide	(1)	3.0
Sodium Sulfamate/Sulfuric acid	(2)	0.5**
Calcium Hypochlorite	(3)	0.5
Sodium Dichlorocyanurate	(4)	0.50
Potassium Bromide	(5)	1.5
Sodium Hydroxide	(6)	0.8
Sodium Triphosphosphate	(7)	1.6
Sodium Acetate	(8)	0.3
Potassium Hydroxide	(9)	0.85
Sodium Octyl Sulfate	(10)	3.00
Dyes/perfume	(11)	0.28
Water	(12)	bal.

\*\*weight equivalent to sulfamic acid content, dry basis

Ingredient	Addition Sequence	wt %
Surfactant	(2)	6.1
Sodium Dichlorocyanurate	(3)	1.2
Melamine	(4)	0.23
Potassium Bromide	(5)	1.0
Tetrapotassium Pyrophosphate	(6)	13.0
Tripotassium Phosphate	(7)	12.0
Sodium Silicate	(8)	0.5
Calcium Carbonate	(9)	39.0
Calcium Oxide	(10)	2.8
Perlite Abrasive	(11)	22.5
Sodium Hydroxide	(12)	1.1
Water	(1) and (13); split 1:1 by weight	bal.

Note 1:

\*\*Surfactant" refers to C8 Alkyl Sulfate, C12-C14 Dimethylamine N-Oxide or a mixture thereof.

What is claimed is:

1. A process for manufacturing a bleaching composition comprising the steps of:

a) admixing a source of hypochlorite and an aminofunctional compound having the formula:

16

RR'NH

wherein R and R' are independently hydrogen, an organic or inorganic unit, and mixtures thereof, provided both R and R' are not both hydrogen, to form a pre-bromine admixture having a pH not exceeding about 11;

b) adding to the pre-bromine admixture a source of bromine to form a bromine addition admixture; and

c) adjusting the pH of the bromine addition admixture to at least about 13 forming a bleaching composition.

2. A process according to claim 1, wherein said aminofunctional compound is selected from the group consisting of:

i) primary aminofunctional compounds selected from sulfamic acid, alkali metal sulfamates, alkaline earth sulfamates, terta-alkylammonium sulfamates, or mixtures thereof;

ii) secondary amine derivatives having the formula:

$$RR'NH \text{ or } (R'')_2NH$$

wherein R, R', and R'' are organic moieties and wherein carbon atoms of said moieties are bonded to NH;

iii) sulfonamides selected from sulfamide, p-toluenesulfonamide, imidodisulfonamide, benzenesulfonamide, alkyl sulfonamides, or mixtures thereof;

iv) melamine, cyanamide, or mixtures thereof;

v) and mixtures thereof.

3. A process according to claim 1, wherein said source of hypochlorite in (a) is selected from the group consisting of chlorine gas, hypochlorous acid, alkali metal hypochlorites, alkaline earth metal hypochlorites, and mixtures thereof.

4. A process according to claim 1 wherein said source of hypochlorite in (a) is introduced by admixing a hypochlorite-liberating compound with a source of aqueous alkali in the presence of the aminofunctional compound such that the final pH of the pre-bromine admixture does not exceed about 11.

5. A process according to claim 1 wherein said source of bromine is selected from the group consisting of bromine, water-soluble bromide salts, water-soluble hypobromite salts, hypobromous acid, and mixtures thereof.

6. A process according to claim 1 wherein the ratio of the number of moles of hypochlorite added in (a) to the number of moles of aminofunctional compound added in (a) is from about 10:1 to about 1:10.

7. A process according to claim 1 wherein the ratio of the number of moles of hypochlorite added in (a) to the number of moles of said source of bromine added in (b) is from about 10:1 to about 1:10.

8. A process according to claim 1 wherein steps (b) and (c) are conducted at a temperature of from about 5° C. to about 80° C.

9. A process according to claim 1, wherein the pH of the pre-bromine admixture of step (a) is not in excess of about 8.

10. A process according to claim 9 wherein the pH of the pre-bromine admixture of step (a) is from about 1 to about 6.9.

11. A process according to claim 1 further comprising the step of adding to the bleaching composition formed in step (c) one or more carriers.

12. A process according to claim 1 further comprising the step of adding to the bleaching composition formed in step (c) one or more adjunct ingredients, said adjunct ingredients selected from the group consisting of surfactants, buffers,

6,037,318

17

builders, chelants, abrasives, perfumes, colorants, dyes, bleach stabilizers, pigments, color speckles, suds suppressors, anti-tarnish agents, anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal agents, anti-redeposition agents, thickeners, solvents, and mixtures thereof.

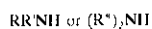
13. A process according to claim 1 wherein said bleaching composition formed in step (c) has from about 0.01% to about 10% available chlorine.

14. A process for manufacturing a bleaching composition comprising the steps of:

- a) admixing a source of hypohalite and an aminofunctional compound, at a temperature of from about 5° C. to about 80° C., to form a pre-bromine admixture having a pH not exceeding about 11;
- b) adding to the pre-bromine admixture, at a temperature of from about 5° C. to about 80° C., a source of bromine to form a bromine addition admixture; and
- c) adjusting the pH of the bromine addition admixture to at least about 13, at a temperature of from about 5° C. to about 80° C., to forming a bleaching composition.

15. A process according to claim 14, wherein said aminofunctional compound is selected from the group consisting of:

- i) primary aminofunctional compounds selected from sulfamic acid, alkali metal sulfamates, alkaline earth sulfamates, terta-alkylammonium sulfamates, or mixtures thereof;
- ii) secondary amine derivatives having the formula:



wherein R, R', and R'' are organic moieties and wherein carbon atoms of said moieties are bonded to NH;

- iii) sulfonamides selected from sulfamide, p-toluenesulfonamide, imidodisulfonamide, benzenesulfonamide, alkyl sulfonamides, or mixtures thereof;
- iv) melamine, cyanamide, or mixtures thereof;
- v) and mixtures thereof.

16. A process according to claim 14, wherein said source of hypohalite in (a) is selected from the group consisting of chlorine gas, hypochlorous acid, alkali metal hypochlorites, alkaline earth metal hypochlorites, and mixtures thereof.

17. A process according to claim 14 wherein said source of bromine is selected from the group consisting of bromine,

18

water-soluble bromide salts, water-soluble hypobromite salts, hypobromous acid, and mixtures thereof.

18. A process according to claim 14 further comprising the step of adding to the bleaching composition formed in step (c) one or more carriers or one or more adjunct ingredients, said adjunct ingredients selected from the group consisting of surfactants, buffers, builders, chelants, abrasives, perfumes, colorants, dyes, bleach stabilizers, pigments, color speckles, suds suppressors, anti-tarnish agents, anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal agents, anti-redeposition agents, thickeners, solvents, and mixtures thereof.

19. A process according to claim 14 wherein said bleaching composition formed in step (c) has from about 0.01% to about 10% available chlorine.

20. A process for manufacturing a bleaching composition comprising the steps of:

- a) admixing a source of hypohalite, said source of hypohalite is selected from the group consisting of alkali metal hypochlorites, alkali earth metal hypochlorites, and mixtures thereof, and an aminofunctional compound, said amino compound selected from the group consisting of sulfamic acid, sulfamate salts thereof, and mixtures thereof, such that the ratio of the number of moles of hypohalite added to the number of moles of aminofunctional compound added is from about 10:1 to about 1:10, to form a pre-bromine admixture having a pH from about 1 to about 6.9;
- b) adding to the pre-bromine admixture a water-soluble bromide salt in an amount such that the ratio of the number of moles of hypohalite added in (a) to the number of moles of water-soluble salt added in (b) is from about 10:1 to about 1:10, to form a bromine addition admixture;
- c) adjusting the pH of the bromine addition admixture to at least about 13 forming a bleaching composition wherein said bleaching composition has from about 0.01% to about 10% available chlorine;
- d) optionally diluting said bleaching composition with a carrier; and
- e) optionally adding to said bleaching composition one or more adjunct ingredients.

\* \* \* \* \*



## **EXHIBIT D**



US006270722B1

(12) **United States Patent**  
**Yang et al.**

(10) **Patent No.:** **US 6,270,722 B1**  
 (45) **Date of Patent:** **Aug. 7, 2001**

(54) **STABILIZED BROMINE SOLUTIONS,  
 METHOD OF MANUFACTURE AND USES  
 THEREOF FOR BIOFOULING CONTROL**

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(\*) **Notice:** Subject to any disclaimer, the term of this  
 patent is extended or adjusted under 35  
 U.S.C. 154(h) by 0 days.

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(22) **Filed:** **Mar. 31, 1999**

(51) **Int. Cl.**<sup>7</sup> ..... **A61L 2/16; C01B 7/09;**  
**D06L 3/06**

(52) **U.S. Cl.** ..... **422/37; 422/6; 8/107;**  
**8/137; 162/1; 423/500; 252/187.2**

(58) **Field of Search** ..... **422/37, 6, 14;**  
**8/107, 137; 162/1, 4; 423/500, 504; 252/187.2,**  
**380**

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(57) **ABSTRACT**

Stabilized bromine solutions are prepared by combining a  
 bromine source and a stabilizer to form a mixture, adding an  
 oxidizer to the mixture, and then adding, an alkaline source  
 to adjust the pH of the mixture to at least 13.

**30 Claims, No Drawings**

US 6,270,722 B1

1

# STABILIZED BROMINE SOLUTIONS, METHOD OF MANUFACTURE AND USES THEREOF FOR BIOFOULING CONTROL

## FIELD OF THE INVENTION

This invention relates generally to water treatment and, more particularly, to stabilized bromine solutions, method of manufacture and uses thereof for biofouling control.

## BACKGROUND OF THE INVENTION

Sodium hypochlorite has been widely used in a variety of industrial and recreational water systems to control biofouling. However, sodium hypochlorite is unstable and must be provided in a stabilized form. There are several methods known in the art for stabilizing hypochlorite (See, e.g., U.S. Pat. Nos. 3,328,294 and 3,767,586).

Bromine is preferred over chlorine for use in water treatment because of its lower volatility and better performance at high pH and amine environments. However, like sodium hypochlorite, sodium hypobromite is unstable in typical storage conditions and must therefore also be provided in a stabilized form. U.S. Pat. Nos. 5,683,654 and 5,795,487, as well as the references disclosed therein, teach various methods for stabilizing sodium hypobromite. The '654 and '487 patents disclose batch methods which utilize sodium hypochlorite and sodium bromide as starting materials, followed by the addition of a stabilizer. WO 97/20909 similarly discloses a process which includes a hypobromite formation step followed by a bromine stabilization step. However, a disadvantage associated with this technique is that unstabilized hypobromite is formed in a separate step at a high concentration and pH. It is known that unstabilized hypobromite degrades quickly under such conditions to form bromate, a non-biocidal compound that is very toxic and a suspected carcinogen.

In addition, WO 97/43392 discloses a process that first forms stabilized chlorine compounds and then converts them to stabilized bromine compounds. However, this type of process is limiting because only hypochlorite-releasing compounds can be used as the oxidizing source.

Therefore, because the demand for stabilized bromine solutions is expected to increase in the future due to its advantages over chlorine, there is a need for other cost-effective methods of manufacturing stabilized bromine which can use a wider range of oxidants and produce a higher strength product at higher yield.

Accordingly, it would be desirable to provide a method of making a stabilized bromine solution which can be carried out as a batch or continuous process and which can produce a higher strength product at higher yield. It would also be desirable to develop a method of making a stabilized bromine solution which is flexible and allows a variety of oxidizers to be utilized.

## SUMMARY OF THE INVENTION

The stabilized bromine solutions of the present invention are prepared by combining a bromine source and a stabilizer to form a mixture, adding an oxidizer to the mixture, and then adding an alkaline source to adjust the pH of the mixture to at least 13.

The inventive method is economically appealing because it can be carried out as a batch or continuous process and because it produces a high-strength stabilized bromine solution at higher yield. The method of preparation is also flexible and allows for the utilization of a variety of oxidizers.

2

## DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method of making stabilized bromine solutions. In accordance with this invention, a bromine source and a stabilizer are combined to form a mixture, an oxidizer is next added to the mixture and then an alkaline source is added to adjust the pH of the mixture to at least 13.

The bromine sources which may be used in the practice of the present invention include hydrobromic acid, bromine chloride, elemental bromine and alkali or alkaline earth metal bromides, such as sodium bromide, potassium bromide and lithium bromide.

The stabilizers which may be employed in this invention have the chemical formula  $R-NH-R^1$ , wherein R and  $R^1$  are selected from the group consisting of  $R^2 CO$ ,  $R^2 SO_2$ ,  $R^2 CF_2$ ,  $R^2 CHF$ , H, OH and  $PO(OH)_2$ , and  $R^2$  is an alkyl group or an aromatic group. Suitable stabilizers include saccharin, urea, thiourea, creatine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine. Sulfamic acid is the most preferred stabilizer.

The oxidizers which may be used include chlorine gas, hypochlorous acid, hypochlorite salt, chlorite, chlorate, elemental bromine, bromine chloride, hydrogen peroxide, persulfate, permanganate and peracetic acid. It is believed that other peroxy compounds can also be used in accordance with this invention.

The alkaline source is preferably an alkali or alkaline earth metal hydroxide. Suitable alkaline sources include sodium hydroxide, lithium hydroxide, potassium hydroxide, magnesium hydroxide and calcium hydroxide.

It is preferred that the molar ratio between the bromine source and the stabilizer be in the range of about 0.2 to 5. The molar ratio between the bromine source and the oxidizer should preferably be in the range of about 0.5 to 2.

The method of the present invention is maintained at a temperature of less than 80° F., and preferably in the range of about 40 to 70° F. The pH of the mixture during the oxidizer addition should be kept below about 7. The present invention can be carried out as either a batch or continuous process.

The stabilized bromine solutions which are prepared in accordance with this invention may be used in a wide variety of commercial applications. These applications include, but are not limited to, the use of the stabilized bromine solution: (1) as the bleaching agent in a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent; (2) as the oxidizing agent in a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached; (3) as the oxidizing and biocidal agent in a method for the control of biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control biofouling; (4) as the oxidizing and biocidal agent in a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface; (5) in a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters; and (6) in a method for controlling biofouling in an aqueous system.

In another embodiment, the invention is a method of preventing biofouling on the surfaces of equipment in contact with an industrial water system. The method comprises adding an effective biofouling controlling amount of a

US 6,270,722 B1

3

stabilized bromine solution to the water system, wherein the solution is prepared by combining a bromine source and a stabilizer to form a mixture, adding an oxidizer to the mixture, and then adding an alkaline source to adjust the pH of the mixture to at least 13.

The types of industrial water systems in which the stabilized bromine solution may be used to prevent biofouling include, but are not limited to, cooling water systems, sweetwater systems, gas scrubber systems, air washer systems, evaporative condensers, pasteurizers, produce sanitizer streams, fire protection water systems and heat exchanger tubes.

It is preferred that the amount of stabilized bromine solution which is added to the industrial water system be in the range of about 0.1 ppm to about 2000 ppm and preferably in the range of about 0.5 ppm to about 500 ppm, based on available bromine concentration. The stabilized bromine solution can be added to the water system by any conventional method, i.e., by slug, intermittently or continuously.

In another embodiment, the invention is a method of making a stabilized bromine solution comprising the steps of selecting a bromine source, and then adding a stabilizer and an oxidizer to the bromine source to form a mixture, wherein the stabilizer and the oxidizer are alternately added to the mixture in an amount sufficient to maintain the pH of the mixture between about 0 and 6.9, more preferably between about 3 and 6.5 and, most preferably, between about 4 and 6. Those skilled in the art will recognize that the amount of stabilizer and oxidizer added can be determined by automatic feed back control based on the pH value of the mixture or simply done manually. At the end of stabilizer and oxidizer addition, an alkaline source is added to the mixture to adjust the pH of the mixture to at least 13. It is preferred that the molar ratio between the bromine source and the stabilizer be in the range of about 0.2 to 5. The molar ratio between the bromine source and the oxidizer should preferably be in the range of about 0.5 to 2. All of the suitable bromine sources, stabilizers, oxidizers and alkaline sources which may be used in accordance with this embodiment of the invention, as well as the temperature conditions, are the same as those described above.

#### EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

##### Example 1

A bench scale experiment was conducted by:

- mixing 6.83 grams of a 45% sodium bromide solution with 3.30 grams of solid sulfamic acid in a 250 ml flask and then immersing the flask in an ice-water bath;
- slowly adding 47.5 grams of a 4.0% sodium hypochlorite solution to the flask while shaking the flask inside the ice-water bath to maintain a low enough temperature so that no bubbling could be seen; and
- slowly adding 4.5 grams of a 50% sodium hydroxide solution to the flask while cooling the flask.

The resulting product was an amber color solution with a pH of 13.5 and total halogen concentration of 6.89% as Br<sub>2</sub> (or 3.06% as available chlorine) as measured by potassium iodide-sodium thiosulfate titration. The ultraviolet (UV) spectra of the product were typical of a stabilized bromine pattern. The free and total DPD calorimetric measurements

4

also suggested that the product was mostly oxidizing bromine compounds (~98%).

##### Example 2

The same process performed above in Example 1 was used to make a higher concentration product using industrial grade sodium hypochlorite in a lab scale.

The product was prepared by:

- mixing 20.5 grams of a 45% sodium bromide solution with 8.70 grams of solid sulfamic acid in a 200 ml flask and then immersing the flask in an ice-water bath to keep the temperature low;
- slowly adding to the mixture 44.0 grams of 14.2% (w/w as available chlorine) industrial grade sodium hypochlorite while shaking the flask in the ice-water bath; and
- adding 12.2 grams of a 50% sodium hydroxide solution to the mixture.

The resulting product was an amber color solution with a pH of 13.5 which contained 15.91% as Br<sub>2</sub> (or 7.07% as available chlorine) according to potassium iodide-sodium thiosulfate titration. The UV spectra of its 1,000 fold dilution were typical of a stabilized bromine profile. The free and total DPD colorimetric measurements also suggested that the product was 100% oxidizing bromine compounds.

##### Example 3

The inventive method was also tested using an in-line approach. Bromine was oxidized and stabilized in a continuous set-up. The process started by preparing two solutions (A and B) in two separate flasks. Solution A was prepared by mixing 60.9 grams of solid sulfamic acid and 143.5 grams of 45% (w/w) sodium bromide solution. Water was added to bring the total volume of Solution A to approximately 375 milliliters. Solution B was prepared by diluting 313.4 grams of 14.2% (w/w as chlorine) sodium hypochlorite with water to 375 milliliters. Solutions A and B were then pumped out of the flasks at a rate of approximately 19 milliliters per minute using a dual pump-head peristaltic pump. The two solutions were blended through a T-tubular connector immersed in an ice-water bath. The mixed solution then traveled through forty feet of 1/4 inch inner diameter PVC tubing immersed in the water bath before discharging into another flask which contained 85.4 grams of 50% (w/w) sodium hydroxide solution.

The resulting product had a total weight of 927 grams. The product had a pH of more than 13.5 and 9.07% as Br<sub>2</sub> (or 4.03% as available chlorine) as measured by potassium iodide-sodium thiosulfate titration. The UV spectra of its 500 fold dilution were typical of a stabilized bromine profile. The free and total DPD calorimetric measurements also suggested that the product was 93% oxidizing bromine compounds.

##### Example 4

A bench scale batch process was also performed using chlorine gas as an oxidizer. A starting solution (Solution C) was prepared by mixing 340 grams of 45% sodium bromide solution, 100 grams of soft water and 144.4 grams of solid sulfamic acid in a one-liter three neck flask. The flask was immersed in an ice-water bath to keep the solution temperature between 10° C. and 25° C. The pH of Solution C was adjusted from about pH 4.0 to about 5.0 with a sodium hydroxide solution (50% w/w). After the addition of sodium hydroxide, the temperature of Solution C was cooled to

## US 6,270,722 B1

5

about 10° C. Chlorine gas was then bubbled into Solution C at a steady rate. While the chlorine gas was added to Solution C, the pH was maintained from about pH 4.0 to about 5.0 with a concentrated sodium hydroxide solution and the temperature was maintained from about 10° C. to about 25° C. Chlorine gas was added until the solution contained about 10.59% available chlorine according to potassium iodide-sodium thiosulfate titration. Additional sodium hydroxide solution was added to raise the product pH to about 13.5. Any mixed salts formed during the reaction were removed by filtration.

The resulting product was an amber color solution with a pH of about 13.5 and contained about 21.85% as Br<sub>2</sub> (or 9.71% as available chlorine) as measured by potassium iodide-sodium thiosulfate titration. The UV spectra of the product were typical of a stabilized bromine pattern. The free and total DPD calorimetric measurements also suggested that the product was mostly oxidizing bromine compounds (~97%).

## Example 5

Another bench scale experiment was conducted by mixing 75.0 grams of a 45% sodium bromide solution with 10 grams of water in a 500 ml flask and then immersing the flask in an ice-water bath. Approximately 1 gram of sulfamic acid was added to the 500 ml flask to lower the solution pH to less than 1, and then 24.0% (weight percent as available chlorine) sodium hypochlorite solution (HyPure-N available from Olin Corporation of Cheshire, Conn.) was slowly dripped into the flask while the solution was mixed with a magnetic stir bar. When the pH increased to about 6, a small portion of sulfamic acid was added again to lower the pH back to between 2 and 3. The pH of the solution was controlled between 2 to 6 by alternating the addition of the sodium hypochlorite solution and sulfamic acid. The total amount of sulfamic acid added was 35.0 grams and the total amount of the sodium hypochlorite solution was 101.6 grams. The entire process was conducted in the solution temperature range of about 57 to 68° F. 31.75 grams of 50% sodium hydroxide solution were then slowly added to the flask while maintaining the solution temperature below 68° F.

The resulting product was an amber color solution with a pH of 13.3 and total halogen concentration of 20.75% as Br<sub>2</sub> (or 9.22% as available chlorine) as measured by potassium iodide-sodium thiosulfate titration. The UV spectra of the product were typical of a stabilized bromine pattern.

## Example 6

A solution of sodium hypochlorite (CLOROX®) and two solutions of stabilized sodium hypobromite (one solution was STABREX™, available from Nalco Chemical Company of Naperville, Ill. and the other solution was prepared as described above in Example 4) were each diluted and then added to cooling water in order to achieve a one ppm total halogen residual (as chlorine). The synthetic cooling water contained 10 ppm NH<sub>4</sub>Cl and approximately 10<sup>6</sup> cells/ml of mixed cooling water bacteria. Aliquots of the treated samples were extracted at 0, 0.5, 1, 2, 5, 10, 20, 30, 45, and 60 minutes into phosphate buffered dilution blanks containing a halogen neutralizer (0.05% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) and then enumerated on a tryptic soy agar plate. Both solutions of stabilized sodium hypobromite were much more effective biocidally in the presence of NH<sub>4</sub>Cl than sodium hypochlorite (See Table 1 below). In addition, the efficacy of the

6

stabilized sodium hypobromite solution prepared in Example 4 was identical to Nalco's STABREX™ product.

TABLE 1

Log <sub>10</sub> Viable Bacteria Cells/ml.				
Time (Minutes)	Control	Unstabilized sodium hypochlorite (CLOROX®)	Nalco's STABREX™ product	Stabilized sodium hypobromite (from Example 4)
0	6.07	6.07	6.07	6.07
0.5	—	6.05	6.06	6.07
1	—	6.03	4.78	4.59
2	—	6.07	2.48	2.48
5	6.02	6.12	<1	<1
10	6.09	6.03	<1	<1
20	6.07	5.52	<1	<1
30	6.04	5.08	<1	<1
45	6.09	3.87	<1	<1
60	6.17	2.00	<1	<1

While the present invention is described above in connection with preferred or illustrative embodiments, these embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover all alternatives, modifications and equivalents included within its spirit and scope, as defined by the appended claims.

What is claimed is:

1. A method of making a stabilized bromine solution comprising the steps of:

- a. combining a bromine source and a stabilizer to form a mixture;
- b. adding an oxidizer to the mixture; and
- c. adding an alkaline source to the mixture to adjust the pH of the mixture to at least 13.

2. The method of claim 1 wherein the bromine source is selected from the group consisting of hydrobromic acid, bromine chloride, elemental bromine, alkali earth metal bromides and alkaline earth metal bromides.

3. The method of claim 1 wherein the stabilizer has the chemical formula R—NH—R<sup>1</sup>, wherein R and R<sup>1</sup> are selected from the group consisting of R<sup>2</sup> CO, R<sup>2</sup> SO<sub>2</sub>, R<sup>2</sup> CF<sub>2</sub>, R<sup>2</sup> CHF, H, OH and PO(OH)<sub>2</sub>, and R<sup>2</sup> is an alkyl group or an aromatic group.

4. The method of claim 1 wherein the stabilizer is selected from the group consisting of saccharin, urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

5. The method of claim 1 wherein the stabilizer is sulfamic acid.

6. The method of claim 1 wherein the oxidizer is selected from the group consisting of chlorine gas, hypochlorous acid, hypochlorite salt, chlorite, chlorate, elemental bromine, bromine chloride, hydrogen peroxide, persulfate, permanganate and peracetic acid.

7. The method of claim 1 wherein the alkaline source is selected from the group consisting of alkali earth metal hydroxides and alkaline earth metal hydroxides.

8. The method of claim 1 wherein the alkaline source is selected from the group consisting of sodium hydroxide, lithium hydroxide, potassium hydroxide, magnesium hydroxide and calcium hydroxide.

9. The method of claim 1 wherein the molar ratio between the bromine source and the stabilizer is in the range of about 0.2 to 5.

10. The method of claim 1 wherein the molar ratio between the bromine source and the oxidizer is in the range of about 0.5 to 2.

US 6,270,722 B1

7

11. The method of claim 1 wherein steps a, b and c are maintained at a temperature of less than 80° F.

12. The method of claim 1 wherein steps a, b and c are maintained in the temperature range of about 40 to 70° F.

13. The method of claim 1 wherein step b is maintained at a pH below about 7.

14. A stabilized bromine solution produced by the method of claim 1.

15. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprising using as the bleaching agent the stabilized bromine solution of claim 14.

16. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprising using as the oxidizing agent the stabilized bromine solution of claim 14.

17. In a method for the control of biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control biofouling, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 14.

18. In a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 14.

19. In a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters, the improvement comprising adding to the produced oil field waters an effective biofouling controlling amount of the stabilized bromine solution of claim 14.

20. A method of controlling biofouling in an aqueous system which comprises adding to the aqueous system an effective, biofouling controlling amount of the stabilized bromine solution of claim 14.

21. A method of preventing biofouling on the surfaces of equipment in contact with an industrial water system which comprises adding to the water system an effective biofouling controlling amount of a stabilized bromine solution, said solution having been prepared by the steps of:

- a. combining a bromine source and a stabilizer to form a mixture;

8

- b. adding an oxidizer to the mixture; and

- c. adding an alkaline source to the mixture to adjust the pH of the mixture to at least 13.

22. The method of claim 21 wherein the industrial water system is selected from the group consisting of a cooling water system, sweetwater system, gas scrubber system, air washer system, evaporative condenser, pasteurizer, produce sanitizer stream, fire protection water system and heat exchanger tube.

23. The method of claim 21 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.1 to about 2000 ppm as available bromine.

24. The method of claim 21 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.5 to about 500 ppm as available bromine.

25. A method of making a stabilized bromine solution comprising the steps of:

- a. selecting a bromine source;
- b. adding a stabilizer and an oxidizer to the bromine source to form a mixture, wherein the stabilizer and the oxidizer are alternately added to the mixture in an amount sufficient to maintain the pH of the mixture between about 0 and 6.9; and
- c. adding an alkaline source to the mixture to adjust the pH of the mixture to at least 13.

26. The method of claim 25 wherein the pH of step b is between about 3 and 6.5.

27. The method of claim 25 wherein the pH of step b is between about 4 and 6.

28. The method of claim 25 wherein the molar ratio between the bromine source and the stabilizer is in the range of about 0.2 to 5.

29. The method of claim 25 wherein the molar ratio between the bromine source and the oxidizer is in the range of about 0.5 to 2.

30. A stabilized bromine solution produced by the method of claim 25.

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## **EXHIBIT E**



US006669904B1

(12) **United States Patent**  
**Yang et al.**

(10) **Patent No.:** **US 6,669,904 B1**  
(45) **Date of Patent:** **Dec. 30, 2003**

(54) **STABILIZED BROMINE SOLUTIONS,  
METHOD OF MAKING AND USES  
THEREOF FOR BIOFOULING CONTROL**

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(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(h) by 0 days.

(21) Appl. No.: **09/920,399**

(22) Filed: **Aug. 1, 2001**

#### **Related U.S. Application Data**

(63) Continuation-in-part of application No. 09/283,122, filed on  
Mar. 31, 1999, now Pat. No. 6,270,722.

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(52) U.S. Cl. .... **422/37**; 422/7; 422/14;  
423/500; 252/186.36; 252/187.2; 210/754;  
162/70

(58) Field of Search ..... 422/37, 7, 14;  
423/462, 500; 210/754; 252/186.36, 187.2;  
162/70

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#### (57) **ABSTRACT**

Stabilized bromine solutions are prepared by combining a  
bromine source and a stabilizer to form a mixture, and then  
adding an oxidizer to the mixture.

**20 Claims, No Drawings**

US 6,669,904 B1

1

# STABILIZED BROMINE SOLUTIONS, METHOD OF MAKING AND USES THEREOF FOR BIOFOULING CONTROL.

## REFERENCE TO RELATED PATENT

This application is a continuation-in-part of U.S. Ser. No. 09/283,122, filed on Mar. 31, 1999 now U.S. Pat. No. 6,270,722.

## FIELD OF THE INVENTION

This invention relates generally to water treatment and, more particularly, to stabilized bromine solutions, method of making and uses thereof for biofouling control.

## BACKGROUND OF THE INVENTION

Sodium hypochlorite has been widely used in a variety of industrial and recreational water systems to control biofouling. However, sodium hypochlorite is unstable and must be provided in a stabilized form. There are several methods known in the art for stabilizing hypochlorite (See, e.g., U.S. Pat. Nos. 3,328,294 and 3,767,586).

Bromine is preferred over chlorine for use in water treatment because of its lower volatility and better performance at high pH and amine environments. However, like sodium hypochlorite, sodium hypobromite is unstable in typical storage conditions and must therefore also be provided in a stabilized form. U.S. Pat. Nos. 5,683,654 and 5,795,487, as well as the references disclosed therein, teach various methods for stabilizing sodium hypobromite. The '654 and '487 patents disclose batch methods which utilize sodium hypochlorite and sodium bromide as starting materials, followed by the addition of a stabilizer. WO 97/20909 similarly discloses a process which includes a hypobromite formation step followed by a bromine stabilization step. However, a disadvantage associated with this technique is that unstabilized hypobromite is formed in a separate step at a high concentration and pH. It is known that unstabilized hypobromite degrades quickly under such conditions to form bromate, a non-biocidal compound that is very toxic and a suspected carcinogen.

In addition, WO 97/43392 discloses a process that first forms stabilized chlorine compounds and then converts them to stabilized bromine compounds. However, this type of process is limiting because only hypochlorite-releasing compounds can be used as the oxidizing source.

Therefore, because the demand for stabilized bromine solutions is expected to increase in the future due to its advantages over chlorine, there is a need for other cost-effective methods of making stabilized bromine which can use a wider range of oxidants.

Accordingly, it would be desirable to provide a method of making a stabilized bromine solution which can be carried out as a batch or continuous process right at the site of the commercial application. It would also be desirable to develop a method of making a stabilized bromine solution which is flexible and allows a variety of oxidizers to be utilized.

## SUMMARY OF THE INVENTION

The stabilized bromine solutions of the present invention are prepared by combining a bromine source and a stabilizer to form a mixture, and then adding an oxidizer to the mixture.

The inventive method is economically appealing because it can be carried out as a batch or continuous process at the

2

commercial application site, thereby eliminating the need to store and transport the stabilized bromine solutions. The method of preparation is also flexible and allows for the utilization of a variety of oxidizers.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method of making stabilized bromine solutions. In accordance with this invention, a bromine source and a stabilizer are combined to form a mixture, and then an oxidizer is added to the mixture.

The bromine sources which may be used in the practice of the present invention include hydrobromic acid, and alkali or alkaline earth metal bromides, such as sodium bromide, potassium bromide and lithium bromide.

The stabilizers which may be employed in this invention have the chemical formula  $R-NH-R^1$ , wherein R and  $R^1$  are selected from the group consisting of  $R^2CO$ ,  $R^2SO_2$ ,  $R^2CF_2$ ,  $R^2CHF$ , H, OH and  $PO(OH)_2$ , and  $R^2$  is an alkyl group or an aromatic group. Suitable stabilizers include saccharin, urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoethanolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid and its alkali or alkaline earth metal salts, organic sulfamates and melamine. Sulfamic acid and its alkali or alkaline earth metal salts are the most preferred stabilizers.

Optionally, other water treatment chemicals, such as tracing compounds, surfactants, corrosion inhibitors and scale inhibitors, can be added to the bromine/stabilizer mixture.

The oxidizers which may be used include chlorine gas, hypochlorous acid, hypochlorite salt, chlorite, chlorate, elemental bromine, bromine chloride, hydrogen peroxide, persulfate, permanganate and peracetic acid. Chlorine gas, hypochlorous acid and hypochlorite salt are the most preferred oxidizers. It is believed that other peroxy compounds can also be used in accordance with this invention.

The stabilized bromine solutions which are prepared in accordance with this invention can be prepared at the site of the commercial application. This eliminates the need to store and transport the stabilized bromine solutions and thus the need for adding caustic to adjust the pH and extend the shelf life of the solutions. The present invention can be carried out as either a batch or continuous process.

It is preferred that the molar ratio between the bromine source and the stabilizer be in the range of about 0.1 to 10. The molar ratio between the bromine source and the oxidizer should preferably be in the range of about 0.2 to 5.

The stabilized bromine solutions which are prepared in accordance with this invention may be used in a wide variety of commercial applications. These applications include, but are not limited to, the use of the stabilized bromine solution: (1) as the bleaching agent in a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent; (2) as the oxidizing agent in a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached; (3) as the oxidizing and biocidal agent in a method for the control of biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control biofouling; (4) as the oxidizing and biocidal agent in a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface; (5) in a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field waters; (6) in

US 6,669,904 B1

3

a method for controlling biofouling in an aqueous system; (7) in a method for controlling biofouling in pulp and paper manufacturing process water and process chemicals; and (8) in a method for controlling microbial growth in an aqueous stream used for transporting or processing food products and on food surfaces and equipment surfaces that come in contact with the aqueous stream.

In another embodiment, the invention is a method of preventing biofouling on the surfaces of equipment in contact with an industrial water system. The method comprises adding an effective biofouling controlling amount of a stabilized bromine solution to the water system, wherein the solution is prepared by combining a bromine source and a stabilizer to form a mixture, and then adding an oxidizer to the mixture.

The types of industrial water systems in which the stabilized bromine solution may be used to prevent biofouling include, but are not limited to, cooling water systems, sweetwater systems, gas scrubber systems, air washer systems, evaporative condensers, pasteurizers, produce sanitizer streams, fire protection water systems and heat exchanger tubes.

It is preferred that the amount of stabilized bromine solution which is added to the industrial water system be in the range of about 0.1 ppm to about 2000 ppm and preferably in the range of about 0.5 ppm to about 500 ppm, based on available chlorine concentration. The stabilized bromine solution can be added to the water system by any conventional method, i.e., by slug, intermittently or continuously.

### EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

#### Example 1

This example demonstrates the impact of caustic addition. It also illustrates that caustic addition is not needed if the inventive stabilized bromine solutions are prepared and used at the site of the commercial application.

Three stabilized bromine formulations were prepared with the only difference being their caustic contents. The formulations underwent an accelerated thermal degradation test at 135° F. and the product actives were determined by potassium-thiosulfate titration at various times. The half lives of the products were calculated from first order decay curves. As shown below in Table 1, the product half lives indicate that the lower the caustic addition, the shorter the shelf life.

TABLE 1

Raw material	Formulation (moles)		
	A	B	C
Sodium hydroxide	0.176	0.628	5.808
Sulfamic acid	0.126	0.126	0.126
Water	0.488	0.488	0.488
Sodium hypochlorite	0.09	0.09	0.09
Sodium bromide	0.09	0.09	0.09
Product half life (days)	1.8	41.3	41.3

4

#### Example 2

A laboratory experiment was conducted at room temperature (70° F.) by:

1. Preparing a mixture (solution A) of sodium bromide and sodium sulfamate to contain 33.3% wt of sodium bromide and 17.4% of sodium sulfamate in water;
2. Adding 0.76 ml of 10.9% wt (as available chlorine) chlorine bleach to 1000 ml of synthetic cooling water containing 225 ppm (as  $\text{CaCO}_3$ ) hardness and 125 ppm (as  $\text{CaCO}_3$ ) total alkalinity (solution B); and
3. Adding 0.241 ml of solution A to solution B to form the final solution.

One milliliter of the final solution was taken at different time points and diluted 100 times in deionized water. The halogen residual concentrations in the diluted solution were determined using Hach's DPD method 80 on a DR-2000 spectrophotometer. Three types of DPD measurements were taken: (1) free halogen residual using free chlorine reagent and read at 20 seconds after the reagent was added to the test solution, (2) total halogen residual using total chlorine reagent, and (3) 3-minute halogen residual using free chlorine reagent and read at 3 minutes after the reagent was added. As discovered by the inventors, the difference between the total halogen residual and 3-minute halogen residual is the concentration of N-chlorosulfamate.

While determining the halogen residual in the solution, another one milliliter of the final solution was taken and added to a flask containing 100 ml of the synthetic cooling water with  $2.4 \times 10^6$  CFU/ml of cooling water mixed culture bacteria. After five minutes of mixing, an aliquot of sample was taken from the flask and neutralized with sodium bisulfite. The surviving bacterial population was enumerated on 3M's aerobic count Petrifilm® media after appropriate dilution. The test results are summarized below in Table 2.

TABLE 2

Time (minutes)	Halogen residual concentration (ppm as avail. Cl <sub>2</sub> )			log reduction of bacterial count
	Free halogen	3-minute free	Total halogen	
10	0.56	0.56	0.92	>6.3
30	0.48	0.60	0.91	>6.3
66	0.57	0.66	0.93	>6.3
135	0.63	0.70	0.93	>6.3
180	0.63	0.76	0.95	>6.3

The results show the effective biocidal performance of the prepared solution. In addition, the solution was found to be stable and there was no reduction of total halogen residual during the test period while the concentration of N-chlorosulfamate decreased with an increase in the N-bromosulfamate concentration.

While the present invention is described above in connection with preferred or illustrative embodiments, these embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover all alternatives, modifications and equivalents included within its spirit and scope, as defined by the appended claims.

What is claimed is:

1. A method of making a stabilized bromine solution comprising the steps of:
  - a. combining a bromine source and a stabilizer to form a mixture; and
  - b. adding an oxidizer to the mixture, wherein the oxidizer is selected from the group consisting of chlorine gas, hypochlorous acid and hypochlorite salt.

US 6,669,904 B1

5

2. The method of claim 1 wherein the bromine source is selected from the group consisting of hydrobromic acid, alkali earth metal bromides and alkaline earth metal bromides.

3. The method of claim 1 wherein the stabilizer has the chemical formula  $R-NH-R^1$ , wherein R and  $R^1$  are selected from the group consisting of  $R^2CO$ ,  $R^2SO_2$ ,  $R^2CF_2$ ,  $R^2CHF$ , H, OH and  $PO(OH)_2$ , and  $R^2$  is an alkyl group or an aromatic group.

4. The method of claim 1 wherein the stabilizer is selected from the group consisting of saccharin, urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, monoctumolamine, diethanolamine, organic sulfonamides, biuret, sulfamic acid and its alkali or alkaline earth metal salts, organic sulfamates and melamine.

5. The method of claim 1 wherein the stabilizer is selected from the group consisting of sulfamic acid and its alkali or alkaline earth metal salts.

6. The method of claim 1 wherein the molar ratio between the bromine source and the stabilizer is in the range of about 0.1 to 10.

7. The method of claim 1 wherein the molar ratio between the bromine source and the oxidizer is in the range of about 0.2 to 5.

8. A stabilized bromine solution produced by the method of claim 1.

9. In a method for the laundering of soiled garments in which the soiled garments are washed in an aqueous media containing a detergent and a bleaching agent, the improvement comprising using as the bleaching agent the stabilized bromine solution of claim 8.

10. In a method for the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent, the improvement comprising using as the oxidizing agent the stabilized bromine solution of claim 8.

11. In a method for the control of biofouling in a recreational water system in which an oxidizing and biocidal agent is added to control biofouling, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 8.

12. In a method for the control of biofouling on a hard surface in which an oxidizing and biocidal agent is applied to the surface to control biofouling on the surface, the improvement comprising using as the oxidizing and biocidal agent the stabilized bromine solution of claim 8.

13. In a method for the control of biofouling occurring on the surfaces of equipment in contact with produced oil field

6

waters, the improvement comprising adding to the produced oil field waters an effective biofouling controlling amount of the stabilized bromine solution of claim 8.

14. A method of controlling biofouling in an aqueous system which comprises adding to the aqueous system an effective, biofouling controlling amount of the stabilized bromine solution of claim 8.

15. A method of controlling biofouling in pulp and paper manufacturing process water and process chemicals which comprises adding to the process water an effective, biofouling controlling amount of the stabilized bromine solution of claim 8.

16. A method of controlling microbial growth in an aqueous stream used for transporting or processing food products and on food surfaces and equipment surfaces that come in contact with the aqueous stream which comprises adding to the aqueous stream an effective, microbial growth controlling amount of the stabilized bromine solution of claim 8.

17. A method of preventing biofouling on the surfaces of equipment in contact with an industrial water system which comprises adding to the water system an effective biofouling controlling amount of a stabilized bromine solution, said solution having been prepared by the steps of:

- a. combining a bromine source and a stabilizer to form a mixture; and
- b. adding an oxidizer to the mixture, wherein the oxidizer is selected from the group consisting of chlorine gas, hypochlorous acid and hypochlorite salt.

18. The method of claim 17 wherein the industrial water system is selected from the group consisting of a cooling water system, sweetwater system, gas scrubber system, air washer system evaporative condenser, pasteurizer, produce sanitizer stream, fire protection water system and heat exchanger tube.

19. The method of claim 17 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.1 to about 2000 ppm as available chlorine.

20. The method of claim 17 wherein the stabilized bromine solution is added to the industrial water system in an amount of from about 0.5 to about 500 ppm as available chlorine.

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